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## MIXED MEDIA FILTERS FOR AIRCREW BREATHING SYSTEMS

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Myrtle Creek, Oregon 97457

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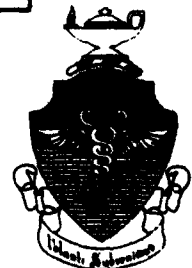
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# NOTICES

This final report was submitted by Umpqua Research Company, Myrtle Creek, Oregon 97457, under contract F33615-76-C-0603, job order 7930-11-08, with the USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas. Dr. Kenneth G. Ikels (USAFSAM/VNL) was the Laboratory Project Scientist-in-Charge.


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This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
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mixtures could not be substantiated. A procedure was developed, however, for coating granular charcoal with a thin layer of silica gel, which produces an essentially dustfree product. Limited testing showed improved performance over conventional charcoal.

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## MIXED MEDIA FILTERS FOR AIRCREW BREATHING SYSTEMS

### INTRODUCTION

This program arose from general and specific needs. The general need is to expand, extend, and improve dryer/filter systems for use in aircraft and/or other Air Force breathing systems. This need is becoming increasingly important because of concern about the quality of air/oxygen required by USAF personnel in highly specialized conditions. The specific need is a response to a potential problem resulting from chemically generated oxygen being produced from contaminated intake air. The condition may create a safety as well as a health hazard.

The scope of this program was a comprehensive experimental study of mixed silica gel and charcoal for use as a dryer/filter system for oxygen purification. The study included (1) the investigation of simple mixtures of silica gel and charcoal, and (2) the product of precipitation of charcoal dispersed in solutions of sodium silicate. In each case, sorbent concentrations were varied such that water vapor adsorption, contaminant adsorption, flammability, and regeneration criteria were established.

The results of the program are presented in this report. Previously reported performance advantages of coprecipitated charcoal/silica gel materials over simple mixtures could not be substantiated. In addition, the coprecipitated materials could not be manufactured in a form with enough physical strength for use in operational equipment.

A procedure was developed for coating granular charcoal with a thin layer of silica gel. This produced an essentially dustfree charcoal product. Limited testing showed no impairment in adsorption properties, and one formulation showed improved performance over conventional charcoal.

### MATERIAL PREPARATION

#### Coprecipitation of Charcoal and Silica Gel (Carbogel)

The coprecipitation product of powdered activated charcoal and silica gel was first described by Puri et al. (1). In their study, powdered activated charcoal was mixed with a sodium silicate solution with a density of 1.185 (approximately 50%). This mixture was stirred, and 1 N HCl was added by drops until the mixture was permanently acidic. The resulting slurry was then washed with distilled water and dried.

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<sup>1</sup>B. R. Puri et al. Studies in properties of charcoal-silica mixed adsorbent systems. J Sci Ind Res 21D:158-161 (1962).

Our first efforts to manufacture carbogels duplicated the procedure described by Puri et al. Initially, we precipitated silica gel by starting with 50 ml of a 50% solution of sodium silicate, MCB SX755 CB751, and adding by drops a 1 N solution of HCl while stirring. A gel formed after 80 ml were added. Approximately 110 ml were required for permanent acidity. Subsequent washing and drying yielded a fine white powder, which has little use in a packed bed. The problem at this point was to develop a procedure to manufacture a crystalline product. After some trial and error, we developed such a procedure.

A somewhat unusual phenomenon occurs when 110 ml of 1 N HCl are rapidly added and mixed with 50 ml of 50% sodium silicate. (This is the mixture eventually arrived at during the dropwise addition that produces a gel.) When the two are mixed rapidly, no precipitate forms, and none forms after standing several days. Slow drying in an oven at 353K (80°C) eventually yields a gel which, upon further drying, produces yellow crystals. After gradual rehumidification, misting with a spray bottle, and final washing to a specific conductance below 100  $\mu$ mho/cm, the yellow disappears. Drying and regeneration at 473K (200°C) with a dry purge yields a product that compares favorably with commercial silica gel.

We attempted to manufacture carbogels (identified as Batch 2, or crystallized silica gel) by the above procedure after mixing Barneby-Cheny Type XZ powdered charcoal with the mixture of sodium silicate and HCl. The results were a mixture of very dark silica gel crystals and a black fragile charcoal. The charcoal apparently precipitated out before the gel formed.

After further investigations, we developed a procedure in which the powdered charcoal was added to the sodium silicate/HCl mixture and heated on a stirred hot plate, just below the boiling point, until enough of a gel formed to stop the magnetic stir bar. The gel was dried in a warm oven and then rewetted and washed as before. This produced a fairly firm cake which was broken up and sieved. The resulting particles of 25% and 50% charcoal were fairly strong, but dusted heavily with handling. The 75% charcoal particles were extremely fragile. None of the three products were strong enough to be useful; however, with careful handling they were used to evaluate the moisture and hydrocarbon adsorption properties of the materials.

In another attempt to produce a coprecipitation product, we investigated three methods of coprecipitating silica gel with Barneby-Cheny Type AC charcoal:

- Batch 7 - Adding charcoal to sodium silicate solution, equilibrating overnight, adding HCl, and crystallizing with low heat.
- Batch 8 - Adding charcoal to supersaturated mixture of sodium silicate and HCl, equilibrating overnight, and crystallizing with low heat.
- Batch 9 - Adding charcoal to HCl, equilibrating overnight, adding sodium silicate, and crystallizing with low heat.

During the crystallization process the charcoal remained at the bottom of the container, while crystals of silica gel were formed around and above. The silica gel had a slightly gray color, indicating that a small amount of dust was contained in the crystal structure. The crystals of silica gel were individually sorted from the charcoal after drying.

The resulting charcoal particles were covered with a thin layer of silica gel which made them essentially dustfree with repeated handling. This may prove to be an important development that should be investigated further. Dusting of charcoal beds in gas-handling systems is a major problem with conventional charcoal. Limited tests, reported later, show no change in the adsorption properties, with measurable improvement in the case of Batch 9.

### Test Materials

Most testing was performed on mixtures of commercially obtained silica gel--MCB SX144 L 1083, Grade H type 11--and Barneby-Cheny types AC and MI charcoal. All adsorption tests were conducted in Aviators Breathing Oxygen MIL-0-27210C type 1.

Hydrocarbon mixtures were prepared from:

Acetaldehyde - MCB AX25 2724

Acrolein - MCB AX324 5945

Benzene - Mallinckrodt 1034

Hexane - MCB HX297 US093

Dimethyl methylphosphonate - Aldrich D16,910-2

### WATER ADSORPTION

The water-adsorption characteristics of the various mixed media beds were determined with humidified oxygen at 20%, 50%, 75%, and 95% relative humidities at 303K (30°C).

### Water Adsorption Test Apparatus

The test apparatus is shown in Figure 1. Aviators Breathing Oxygen (ABO) was fed through flow-controlling regulators, needle valve and rotometer, to a fritted-glass tube submerged in a vacuum flask. The flask was contained in a water bath maintained approximately 5K above the desired dewpoint. The stream was then fed through a heated tube to a condenser and separator maintained at the desired dewpoint. The humidified gas then was passed through a coil and fed to a glass gas-absorption tube (mounted in an incubator maintained at 303K) which held the test bed. (The test beds had been preconditioned at 473K (200°C) for at least 1 hour with a dry nitrogen purge.) The exhaust from the bed flowed to an EEG Model 880 dewpoint hygrometer, whose signal was recorded on a Linear Model 550 recorder.

## Water Adsorption Test Results

The test results are presented in moisture breakthrough curves (Figs. 2A-5D) and summarized in Table 1.

In most cases the breakthrough tests were not run to complete breakthrough since the exhaust humidities approached the feed at a very flat asymptotic rate. This part of the curve is of limited value since the dewpoint analyzer has a very poor precision at the higher dewpoints.

Table 1 data include capacities to breakthrough which were calculated from the moisture content of the feed stream. Capacities to other humidities, or dewpoints, may be calculated as the area between the breakthrough curve and the line representing the feed stream. The ultimate capacities listed were calculated by weighing the beds before and after the tests. They are of limited significance since the tests were stopped when the exhaust stream was flattening out; however, in some cases it was still several degrees below the feed dewpoint. Allowing a bed to run several days could increase the ultimate capacity significantly, with very little change in the exit dewpoint.

Table 2 lists the bed weights used at test flows of 150 cm<sup>3</sup>/min. These data may be used to calculate bed capacities at other dewpoints. Bed densities are also included. Compared to silica gel, some charcoal-containing beds show high capacities but much lower bed densities, thus requiring much more volume for similar moisture capacities.

## ORGANIC VAPOR ADSORPTION

Breakthrough curves were obtained with the mixed media beds, using humidified streams of acetaldehyde, acrolein, benzene, hexane, and dimethyl methylphosphonate (DMMP). At the beginning of the program, certified mixtures of the five compounds at 100 ppm in ABO were purchased.

### Organic Vapor Adsorption Test Apparatus

Two types of apparatus were used for the breakthrough tests. The setup used for hexane, benzene, acetaldehyde, and acrolein is shown in Figure 6. When we found that the breakthrough tests were going to take several weeks to complete, we decided to run multiple beds simultaneously in order to complete the program in a reasonable length of time. A technique was developed by which a measured amount of the organic liquid was evaporated into an evacuated oxygen tank by allowing room air to be pulled through a bubbler; thus, the liquid could be vaporized and pass through the lower explosive limit safely. The tank was then backfilled with ABO to approximately the appropriate final pressure and allowed to equilibrate overnight. The pressure was then adjusted by trial and error to yield 100 ppm of the test compound.

The mixture was fed through a flow regulator and meter, through a bubbler maintained at the appropriate dewpoint, and to a manifold inside the 303K (30°C) incubator. The manifold had 15 needle valves that were connected to glass tubes plugged with copper turnings to support the test beds. The only

TABLE 1. MOISTURE CAPACITIES OF CHARCOAL/SILICA GEL MIXTURES AT 303K (30°C).  
(Feed @ 10 bed volumes/minute)

Composition	20% Relative Humidity				50% Relative Humidity			
	Time to breakthrough (h)	Capacity @ breakthrough (%)	Ultimate capacity (%)		Time to breakthrough (h)	Capacity @ breakthrough (%)	Ultimate capacity (%)	
AC Charcoal	0.92	0.9	1.5		0.45	1.0	5.2	
75% AC	2.3	2.1	4.4		1.5	3.2	15.4	
50% AC	1.9	1.8	5.5		1.9	4.0	17.2	
25% AC	6.9	5.2	8.9		4.4	7.6	22.8	
MI Charcoal	0.72	0.9	1.3		0.5	1.4	6.7	
75% MI	2.25	2.6	4.2		1.25	3.3	14.3	
50% MI	2.3	2.2	7.0		2.8	6.0	17.8	
25% MI	8.0	6.1	9.3		4.2	7.4	20.0	
Carbogels								
75% XZ	1.1	2.0	3.6		0.5	2.1	12.8	
50% XZ	3.5	5.1	9.0		2.0	6.8	26.7	
25% XZ	5.4	6.4	11.0		2.9	8.2	34.9	
Silica gels								
Commercial	10.0	6.7	12.1		7.6	12.3	29.9	
Dropwise	3.9	6.8	12.6		---	---	---	
Crystallized	---	---	---		---	---	---	
Silica-gel-coated								
AC Charcoal								
Batch 7	0.40	0.4	1.0		0.2	0.4	9.3	
Batch 8	0.40	0.4	0.8		0.25	0.5	8.5	
Batch 9	0.43	0.4	0.9		0.2	0.4	9.5	

TABLE 1. (Continued)

Composition	75% Relative Humidity			95% Relative Humidity			Bed density (g/cm <sup>3</sup> )
	Time to breakthrough (h)	Capacity @ breakthrough (%)	Ultimate capacity (%)	Time to breakthrough (h)	Capacity @ breakthrough (%)	Ultimate capacity (%)	
AC Charcoal	0.1	0.3	32.1	0.4	1.7	34.9	0.42
75% AC	0.2	0.6	19.4	0.9	3.5	37.3	0.45
50% AC	1.9	5.3	28.3	2.0	7.0	37.1	0.47
25% AC	3.2	8.9	33.2	3.4	10.9	39.9	0.53
MI Charcoal	0.5	2.1	41.9	0.4	2.1	56.7	0.33
75% MI	1.4	5.3	39.6	1.2	5.8	50.0	0.36
50% MI	2.9	9.0	37.2	2.3	9.2	46.9	0.44
25% MI	4.9	12.5	37.1	4.5	4.7	40.3	0.54
Carbogels							
75% XZ	0.45	3.0	25.9	0.6	4.6	37.3	0.22
50% XZ	1.8	8.7	36.1	1.5	8.9	37.6	0.29
25% XZ	3.0	11.7	39.2	2.8	13.7	41.5	0.35
Silica gels							
Commercial	6.8	14.7	35.2	5.7	7.0	37.0	0.60
Dropwise	2.0	11.1	29.5	1.7	2.9	44.6	0.61
Crystallized	6.0	13.7	26.8	5.1	4.3	45.3	0.23
Silica-gel-coated							
AC Charcoal			33.7	0.25	1.0	35.9	0.44
Batch 7	---	----	34.6	0.25	1.0	43.0	0.44
Batch 8	---	----	34.3	0.20	0.8	36.4	0.43
Batch 9	---	----					

TABLE 2. TYPICAL BED WEIGHTS\*

Composition	15-cm <sup>3</sup> -bed weight (g)	Density (g/cm <sup>3</sup> )
AC Charcoal	6.25	0.42
75% AC	6.75	0.45
50% AC	7.0	0.47
25% AC	8.0	0.53
MI Charcoal	5.0	0.33
75% MI	5.4	0.36
50% MI	6.6	0.44
25% MI	8.1	0.54
Carbogels		
75% XZ	3.3	0.22
50% XZ	4.3	0.29
25% XZ	5.2	0.35
Silica gels		
Commercial	9.0	0.60
Dropwise	3.4	0.23
Crystallized	9.2	0.61
Silica-gel-coated		
AC Charcoal		
Batch 7	6.6	0.44
Batch 8	6.6	0.44
Batch 9	6.5	0.43

---

\*Test flows of 150 cm<sup>3</sup>/min.

materials contacting the gas stream were copper, brass, or glass. Flows were monitored from each bed via a rotometer with a rubber stopper that fit the top of the tubes. Effluent samples taken from the beds by a gastight syringe were analyzed by gas chromatography.

When the purchased gas mixture containing DMMP was checked by gas chromatography, no response was obtained. An attempt was made to prepare a mixture by injecting a few microliters of liquid into a 6-liter flask and heating slightly until the drop evaporated. (This procedure was successfully used with the other compounds to produce standard mixtures.) The air in the flask showed no traces of DMMP. Subsequent rinsing of the flask walls with a known quantity of Freon quantitatively recovered the DMMP. Attempts with a Teflon gas bag were also unsuccessful. We concluded that making a stable mixture of DMMP vapor was not feasible.

The test apparatus used for the DMMP breakthrough tests is shown in Figure 7. A stream of ABO was bubbled through DMMP and mixed with the main humidified stream of ABO. The mixed stream was then fed to the manifold which had a total hydrocarbon analyzer connected to one tap. Flows were initially adjusted based on an estimated vapor pressure of DMMP to produce a mixture of 100 ppm at the manifold. Since a standard vapor mixture could not be produced, a solution of DMMP in water was prepared that contained the same amount of DMMP in 2 ml of liquid that 1 ml of gas would contain at 100 ppm. The flow system was operated and adjusted for several days until the level in gas samples from the manifold reached 100 ppm. Gas samples were taken with an all-Teflon gas-sampling syringe. The syringe was flushed with sample several times, and several samples were injected until repetitive results were obtained. This technique was used during the test run, attempting to start with beds that had not broken through and to work up to the higher levels, since it was very difficult to purge the syringe after a high sample. All test beds were preconditioned at 473K (200°C) for at least 1 hour with a dry nitrogen purge.

#### Organic Vapor Adsorption Test Results

The breakthrough curves for the mixed media beds with the five organic compounds are shown in Figures 8A-12C. The most interesting results are those for silica gel with acetaldehyde (Fig. 8D), acrolein (Fig. 9E), benzene (Fig. 10E), and hexane (Fig. 11E). As the silica gel becomes saturated with water, the hydrocarbon is quantitatively displaced, as evidenced by the area of the curve above the feed line compared to the area below the line (expressed as a percent on the figures).

The capacities of the mixed beds for the five hydrocarbons were calculated to breakthrough and to saturation (Table 3). The capacities are roughly correlatable to the amount of charcoal in each mixture, except for DMMP. In this case, the previously observed strong adsorption tendencies appear to apply only to the macro surfaces of the materials since the amount of DMMP adsorbed, as compared to the other hydrocarbons, appears to be more closely related to bed weight than charcoal composition and to silica gel's having a very high capacity.



TABLE 3. ORGANIC VAPOR ADSORPTION CAPACITIES  
(Weight percent at 30°C, 50% RH)

	Acetaldehyde (100 ppm)			Acrolein (100 ppm)			Benzene (100 ppm)			Hexane (80 ppm)			DMMP (100 ppm)		
	At BT*	Ultimate	(%)	At BT*	Ultimate	(%)	At BT*	Ultimate	(%)	At BT*	Ultimate	(%)	At BT*	Ultimate	(%)
AC Charcoal	0.6	3.5		5.6	7.6		15.2	19.3		18.4	22.0		14.4	16.2	
75% AC	0.1	2.3		4.1	6.3		12.8	20.0		13.0	14.6		11.9	14.3	
50% AC	0.1	1.3		2.4	3.9		8.0	10.3		9.6	11.6		10.0	12.5	
25% AC	0.04	0.2		0.8	1.4		2.1	4.0		3.6	6.1		8.9	10.6	
MI Charcoal	1.0	3.6		5.7	7.4		15.5	23.1		23.5	28.5		17.9	20.2	
75% MI	0.8	3.0		2.9	5.9		12.5	16.0		14.8	19.1		16.5	18.7	
50% MI	0.5	1.6		2.9	4.2		9.3	11.9		8.4	11.1		13.5	15.2	
25% MI	0.1	0.3		1.3	1.8		2.7	4.1		3.0	6.5		9.9	11.9	
Carbogels															
75% XZ	0.1	0.2		0.3	2.4		4.9	7.4		7.1	11.8		5.1	8.2	
50% XZ	0.1	0.2		0	1.8		4.6	6.5		4.8	7.7		8.9	9.8	
25% XZ	0.1	0.2		0.8	2.2		0	2.8		2.5	5.5		8.8	11.5	
Commercial silica gel	0.1	0		0.3	0		0.2	0		0.1	0		8.9	10.7	
Silica-gel-coated AC charcoal															
Batch 7	---	---		---	---		14.4	19.4		15.7	20.0		---	---	
Batch 8	---	---		3.0	5.3		14.4	19.4		15.7	20.4		---	---	
Batch 9	---	---		3.1	5.4		16.7	23.4		20.9	23.6		---	---	

\*Breakthrough

The data for the silica-gel-coated AC charcoal show very good performance compared to that of untreated AC charcoal. Batch 9 showed consistently better performance than the untreated.

The very low capacity for acetaldehyde is consistent with qualitative data published by Barneby-Cheny (Bulletin I-642, Columbus, Ohio, 1963).

#### IGNITION/COMBUSTION STUDIES

Ignition/combustion studies were conducted in oxygen on beds composed of 20%, 60%, and 100% charcoal, at 303K (30°C) and 413K (140°C), when they were 50% and 100% saturated with hexane.

#### Ignition/Combustion Test Apparatus

The test beds were supported on glass wool in a glass tube mounted within a combustion tube furnace (Fig. 13). Aviators Breathing Oxygen was metered through the tube and then passed through a Beckman Model 865 infrared analyzer sensitized for CO<sub>2</sub>. A system was provided near the exit of the tube from which samples were taken for analysis of hexane by gas chromatography, and carbon monoxide by indicator tubes (MSA 47134). Bed temperature was monitored by a thermocouple centered approximately 1 cm above the bottom of the bed.

#### Ignition/Combustion Test-Bed Loading

Beds of the appropriate compositions were weighed in aluminum screen baskets, then placed in a sealed container above a pool of n-hexane and allowed to remain for 2 weeks at room temperature. Liquid hexane remained in the container throughout the 2 weeks, at which time it was assumed that the beds were saturated. The beds were then weighed to determine the saturation capacity and used as the saturated samples. Fresh beds were then weighed and placed in individual sealed containers, together with an amount of hexane calculated to be 50% of the saturation capacity. The liquid disappeared overnight. These were allowed to equilibrate 2 days and were then used as the 50% saturated bed. Saturation capacities are shown in Table 4.

TABLE 4. HEXANE CAPACITIES OF MIXED BEDS

Composition	Saturation capacity, %
AC charcoal	28.9
MI charcoal	43.5
20% AC/silica gel	24.3
20% MI/silica gel	26.3
60% AC/silica gel	26.6
60% MI/silica gel	34.0

### Ignition Combustion Test Procedures

At the beginning of a test, the furnace was allowed to equilibrate at the appropriate test temperature, and the tube was purged with oxygen. When the furnace was again at test temperature, the purge was stopped; the bed was poured into the tube and allowed to stand without purging until the core thermocouple reached the test temperature, at which time the purge was started at 10 bed volumes/min. Gas samples were removed and analyzed for hexane at 2-min intervals, with carbon monoxide samples taken at alternate 2 minutes. The test was allowed to run until the hexane concentration fell to below 10% of the initial value.

### Ignition/Combustion Test Results

The most significant result of the testing was that no ignition occurred in any of the samples. Traces of carbon dioxide were observed in the initial few minutes of each sample, the most at 413K (140°C); however, some was also observed from charcoal which contained no hexane. The gas analysis data are summarized in Table 5. The reported values are the maximum observed, which occurred within the first 5 minutes. No carbon monoxide was observed.

### REGENERATION CHARACTERISTICS

The regeneration characteristics of the filter/dryer systems were investigated at charcoal concentrations of 0%, 40%, and 60% with respect to silica gel.

### Test Conditions

Regeneration Test Apparatus--A schematic of the test apparatus is shown in Figure 14. The test beds were supported on copper turnings in the inner annular space of the jacketed test housing. The housing was manufactured from standard copper tubing and was intended to maximize heat transfer to the bed. Ethylene glycol was pumped into the bottom of the outer jacket, up the sides, and down the inner tube, to provide heat transfer surfaces on both sides of the bed as well as preheat (or cooling) to the copper turnings through which the gas streams flowed. The extra efforts to provide efficient heat transfer were necessitated by the short (2 min) time/temperature cycle.

Baths of ethylene glycol were maintained at 298K (25°C) and 418K (145°C) in an attempt to attain bed temperatures of 303K (30°C) and 413K (140°C) during the 2-min cycles. Motor-driven valves and the pumps were activated by a 2-min timer. Solenoid valves were also activated by the timer to flow 150 cm<sup>3</sup>/min of 80 ppm hexane in ABO humidified to 75% RH by a bubbler in a water bath, and a dry mixture of 5% O<sub>2</sub> in N<sub>2</sub> at 1.5 liters/min. The exhaust from the bed was passed through a Beckman Model 400 total hydrocarbon analyzer, and an EEG Model 880 dewpoint analyzer. Each instrument had a Linear Model 550 recorder.

TABLE 5. IGNITION/COMBUSTION TEST DATA

Bed loading	Saturated with Hexane				50% Saturated with Hexane				Fresh Bed	
	30°C		140°C		30°C		140°C		140°C	
	Hexane saturation (%)	CO <sub>2</sub> (%)	Hexane saturation (%)	CO <sub>2</sub> (%)	Hexane saturation (%)	CO <sub>2</sub> (%)	Hexane saturation (%)	CO <sub>2</sub> (%)	CO <sub>2</sub> (%)	
Bed temperature										
Maximum gas composition										
Bed Composition										
AC charcoal	32	<.005	59	0.03	0.2	<.005	7	0.11		0.006
60% AC/silica gel	33	<.005	76	0.05	2.0	<.005	47	.10		---
20% AC/silica gel	38	<.005	78	0.02	7.0	<.005	78	0.04		---
MI charcoal	33	<.005	106	0.16	.1	<.005	25	0.08		0.006
60% MI/silica gel	36	<.005	87	0.10	.27	<.005	40	0.11		---
20% MI/silica gel	37	<.005	81	0.04	4.0	<.005	72	0.03		---

CO &lt; 0.005% all tests

No ignition observed on any test

Temperature Profiles--The required temperature conditions for the regeneration test were a 2-min adsorption cycle at 303K (30°C) and a 2-min regeneration cycle at 413K (140°C). Figure 15 shows temperature profiles of one thermocouple soldered to the tube wall, one placed in the bed immediately adjacent to the wall, and one in the bed at the center of the annular space. The core temperature of a charcoal or silica gel particle would probably respond somewhat slower than the thermocouple bead.

Instrument Responses--Figure 16 shows the response of the hydrocarbon and dewpoint instruments to the adsorption and regeneration gas streams. The timer did not produce a precise 2-min cycle; the adsorption cycle averaged 2 minutes 15 seconds, and the regeneration cycle averaged 1 minute 45 seconds. The hydrocarbon analyzer showed a direct asymptotic response during the 0.15-liter/min adsorption cycle, with a sharp spike due to the pressure pulse when switching to the 1.5-liters/min regeneration flow. Regeneration response was almost instantaneous. The dewpoint analyzer showed a very slow response to the adsorption cycle and hunted when the final point was approached. The spike near the beginning of the regeneration cycle is probably due to residual hunting from the adsorption cycle, and is followed by a fairly rapid decline from the dry regeneration gas flow.

The rapid response of the hydrocarbon analyzer to the regeneration gas shows that the indicated dewpoint lag is caused by slow instrument response rather than by dilution lag due to the plumbing between the bed and the instruments. Figure 17 shows the dewpoint curve plotted as humidity, which is a nonlinear function of dewpoint. The sharper curves indicate even more lag during the adsorption cycle, but somewhat faster response during regeneration.

#### Regeneration Test Results

The intent of the regeneration testing was to establish the point where each regeneration cycle removed as much hexane and water vapor as was added during the adsorption cycle; and then determine the working capacity of the bed at that bed loading, and the breakthrough characteristics.

Completion of the breakthrough tests (Organic Vapor Adsorption section) showed that more than 10 days were required for breakthrough of 50% charcoal beds at 303K (30°C). Consequently we concluded that an excessive length of time would be required to establish regeneration steady-state starting with fresh beds. Tests were conducted by preloading the various beds with hexane in an attempt to arrive at conditions that approximated equilibrium. Moisture equilibrium was established within a matter of minutes for all beds tested. The unloaded silica gel bed also rapidly achieved equilibrium with hexane.

Silica Gel Regeneration Results--Typical regeneration cycles for the silica gel bed are shown in Figure 18. Integration of the area under the regeneration portion, as compared to the area under the feed curve from Figure 16, corrected for flowrate, shows 96% recovery, which is well within the precision of the test instrumentation. Thus it was assumed that equilibrium had been reached at this point, 60-min run time (the test was continued an additional hour with no change in peak characteristics). The hexane concentration of the exhaust at the end of the adsorption cycle appears to approach 5 ppm; however,

the zero of the hydrocarbon analyzer was set with the regeneration gas, and pure oxygen looks like 5 ppm hexane due to a change in flame temperature in the detector.

After replotting the dewpoint curve as humidity, integration of the regeneration curve showed only 80% recovery. The extreme lag in the dewpoint instrument response is the most likely explanation for the lack of agreement for this data. The dewpoint at the end of the adsorption cycle appears to approach 255K (-18°C), however, indicating that it is working effectively. Data from long-term tests confirm equilibrium conditions.

Regeneration Data for 40% MI Charcoal--The initial regeneration test on a bed containing charcoal was conducted on a fresh bed of 40% MI charcoal and allowed to cycle for 18.5 hours. The test was stopped at this time since no appreciable hexane appeared in the regeneration stream. Cycle curves are shown in Figure 19A. This confirms the original assumptions based on the breakthrough data. The dewpoint curves were quite similar to those obtained with silica gel, and did not change throughout the 18.5-h run.

We subsequently decided to try to preload beds with hexane in an attempt to approximate the equilibrium loading. At a later date (not in chronological sequence), another fresh bed of 40% MI was started and liquid hexane was added to the adsorption stream in 10- $\mu$ l increments to a total of 60  $\mu$ l (39.5 mg). After a total of 11 hours, the regeneration peaks appeared to become stable (Fig. 19B). The integrated area of the regeneration peak was approximately 51% of the feed peak. After the illustrated cycle, an adsorption cycle was conducted until the hexane concentration equilibrated at an apparent 4 ppm (actually zero). The moisture curve is essentially identical to that shown for a fresh bed in Figure 19A.

Regeneration Data for 40% AC Charcoal--After the test with the fresh bed that showed no regeneration after 18 hours, we decided to approach equilibrium from the other direction; i.e., start with a saturated bed. A bed of 40% AC charcoal was placed in a sealed container with an amount of hexane calculated to approximate the saturation capacity (approx. 0.7 g). After 24 hours the liquid had evaporated and no hexane odor was evident. This bed was placed in the apparatus and a test started. The initial regeneration peaks reached 7,500 ppm, while the end of the adsorption cycle started at 60 ppm and reached 30 ppm after 30 minutes. The curves in Figure 19C were obtained after 9 hours. The regeneration peak contains approximately 4 times the feed peak, with the adsorption cycle leveling off at an actual 10 ppm hexane. An extended regeneration cycle is essentially identical to other tests. This test was terminated since it appeared that an excessive length of time would be required to reach equilibrium.

Regeneration Data for 60% AC Charcoal--The regeneration test for the 60% AC mixture was conducted with a fresh bed, and 110  $\mu$ l (72.4 mg) of hexane were added in 10- $\mu$ l increments during the early adsorption cycles. The regeneration peaks gradually increased in size over 6 hours. The peaks had the same shape as shown in Figures 19A-C, with the regeneration peak having an area corresponding to 78% of the feed peak. Subsequently the adsorption cycle was allowed to reach steady state which occurred at an indicated 4 ppm (actual

zero). The regeneration cycle was then run for 15 minutes and appeared to stabilize at 105 ppm.

Regeneration Data for 60% MI Charcoal--The 60% MI charcoal was tested with a fresh bed with 90  $\mu$ l (59.4 mg) of hexane added in 10- $\mu$ l increments (as for the 60% AC charcoal) and allowed to run for 10 hours. Before the addition of hexane, an extended adsorption cycle equilibrated at an indicated 5 ppm hexane (actual zero). Immediately after the additions, another extended cycle came to an indicated 4 ppm, as did a third at the end of the 10 hours. At this time the regeneration peak had increased to 176% of a feed peak. An extended regeneration peak at this time leveled off at 120 ppm.

Regeneration Test Summary--With the exception of the silica gel test, regeneration data were not collected under equilibrium adsorption-desorption conditions. The data summarized in Table 6, however, provide enough information to predict the behavior of the systems under conditions of interest. The 40% MI charcoal bed that was started fresh and regenerated for 18 hours without any evidence of hexane in the regeneration step, confirms an extremely long, useful life as predicted during the breakthrough tests. Additionally, the tests in which the beds were preloaded with hexane to the point that more hexane was being regenerated than was adsorbed each cycle, showed adsorption characteristics essentially identical with those of fresh beds. In all cases, the effluent from the beds were in the indicated range of 3.5 to 5 ppm hexane, which is actually less than 1 ppm.

TABLE 6. REGENERATION DATA SUMMARY

Bed composition	Hexane added (mg)	Regeneration adsorption (%)	Time (h)	Hexane adsorption equilibrium (ppm)
100% Silica gel	0	96	1	<1
40% MI charcoal	0	0	18	<1
40% MI charcoal	39.5	51	11	<1
40% AC charcoal	700	408	9	10
60% AC charcoal	72.4	78	6	<1
60% MI charcoal	0	0	0.5	<1
60% MI charcoal	59.4	0	2	<1
60% MI charcoal	50.4	176	10	<1

The silica gel test reached equilibrium rapidly, which was expected due to the low capacity for hexane determined earlier.

The moisture regeneration data, although obtained under equilibrium conditions, do not clearly reflect the actual profiles because of the slow response of the dewpoint analyzer. The later portions of the adsorption cycles do approach a very low dewpoint, however, thus indicating that satisfactory regeneration is occurring.

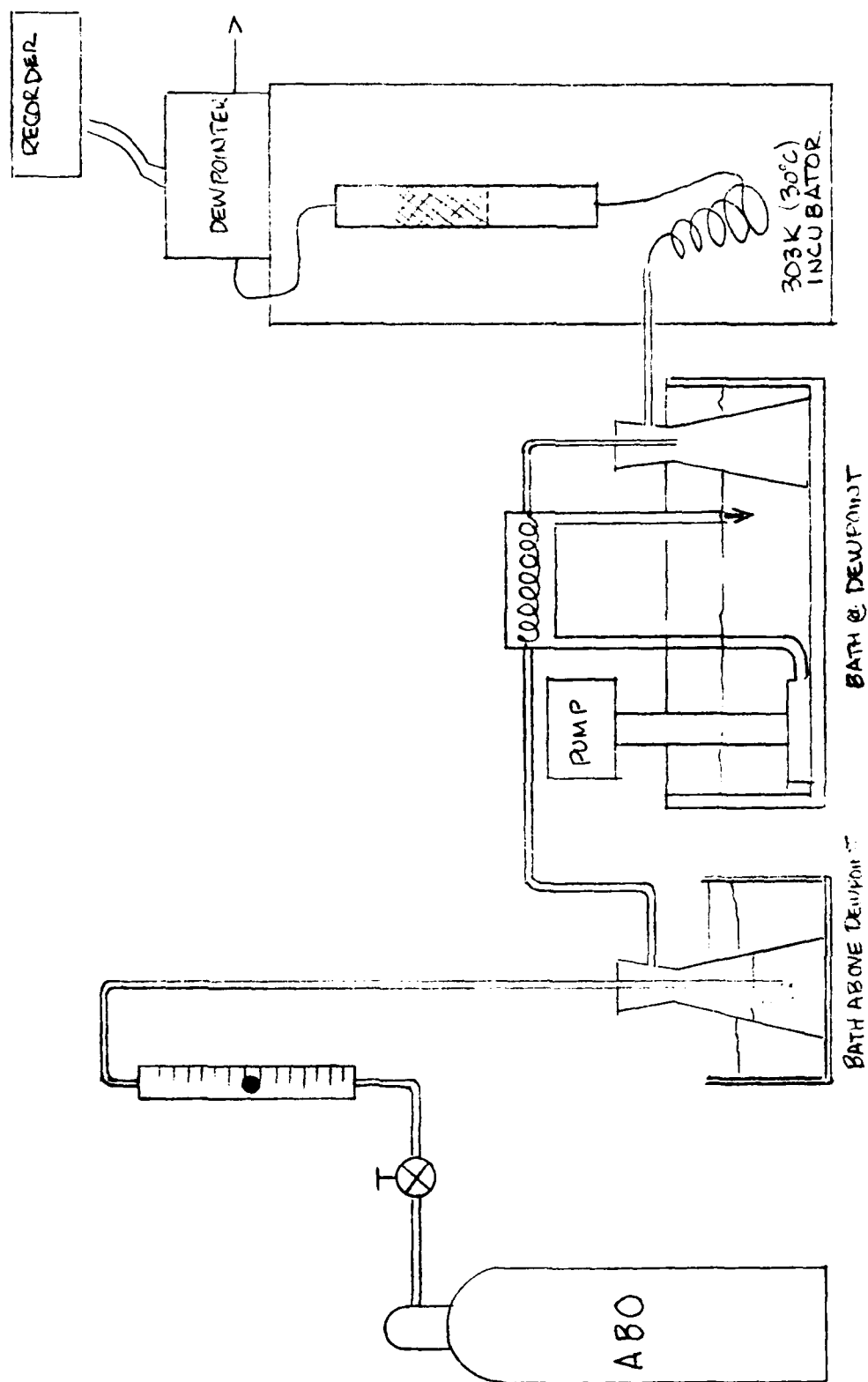


Figure 1. Water adsorption apparatus.



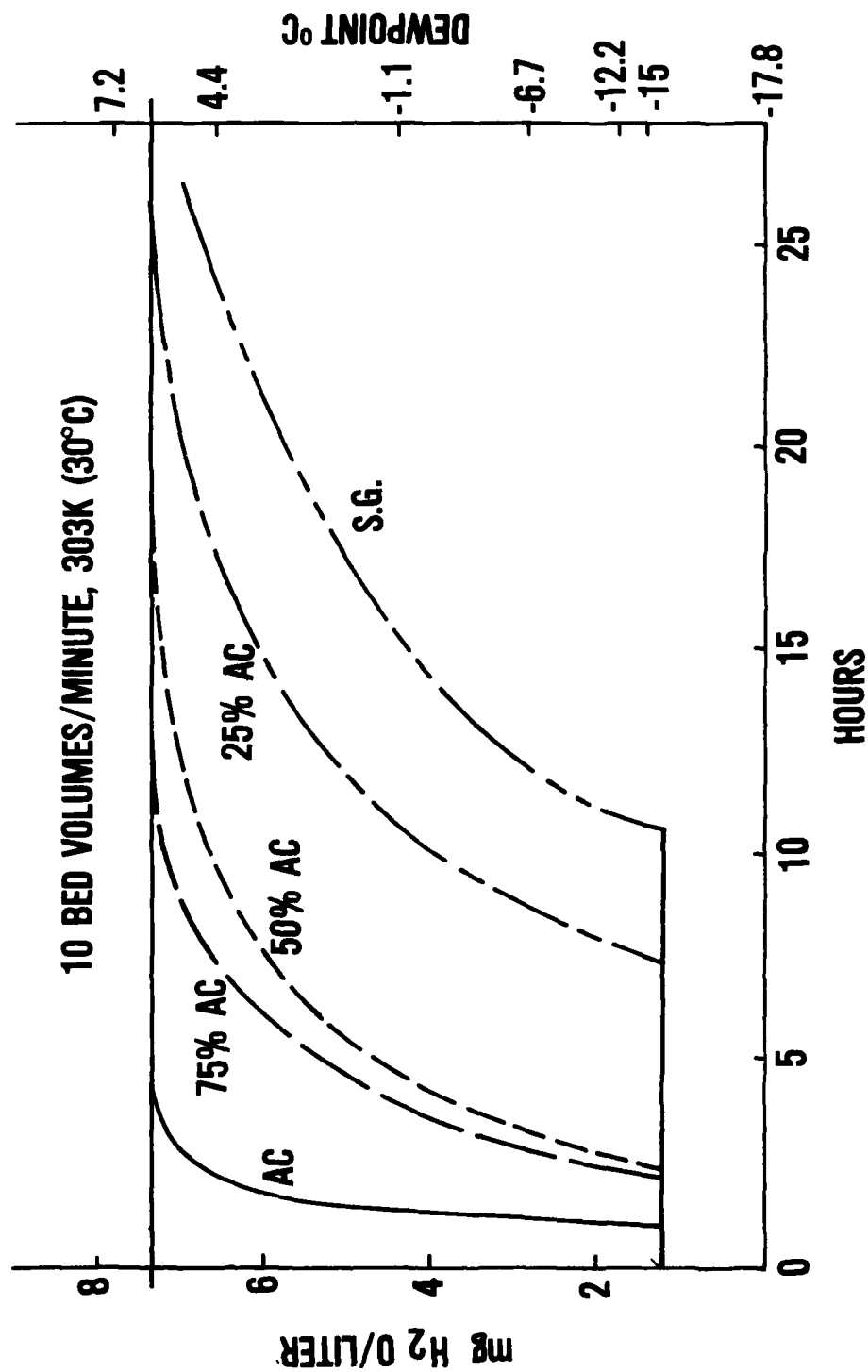


Figure 2A. Moisture breakthrough curves, RH 20%: AC charcoal/silica gel mixtures.

10 BED VOLUMES/MINUTE, 303K (30°C)

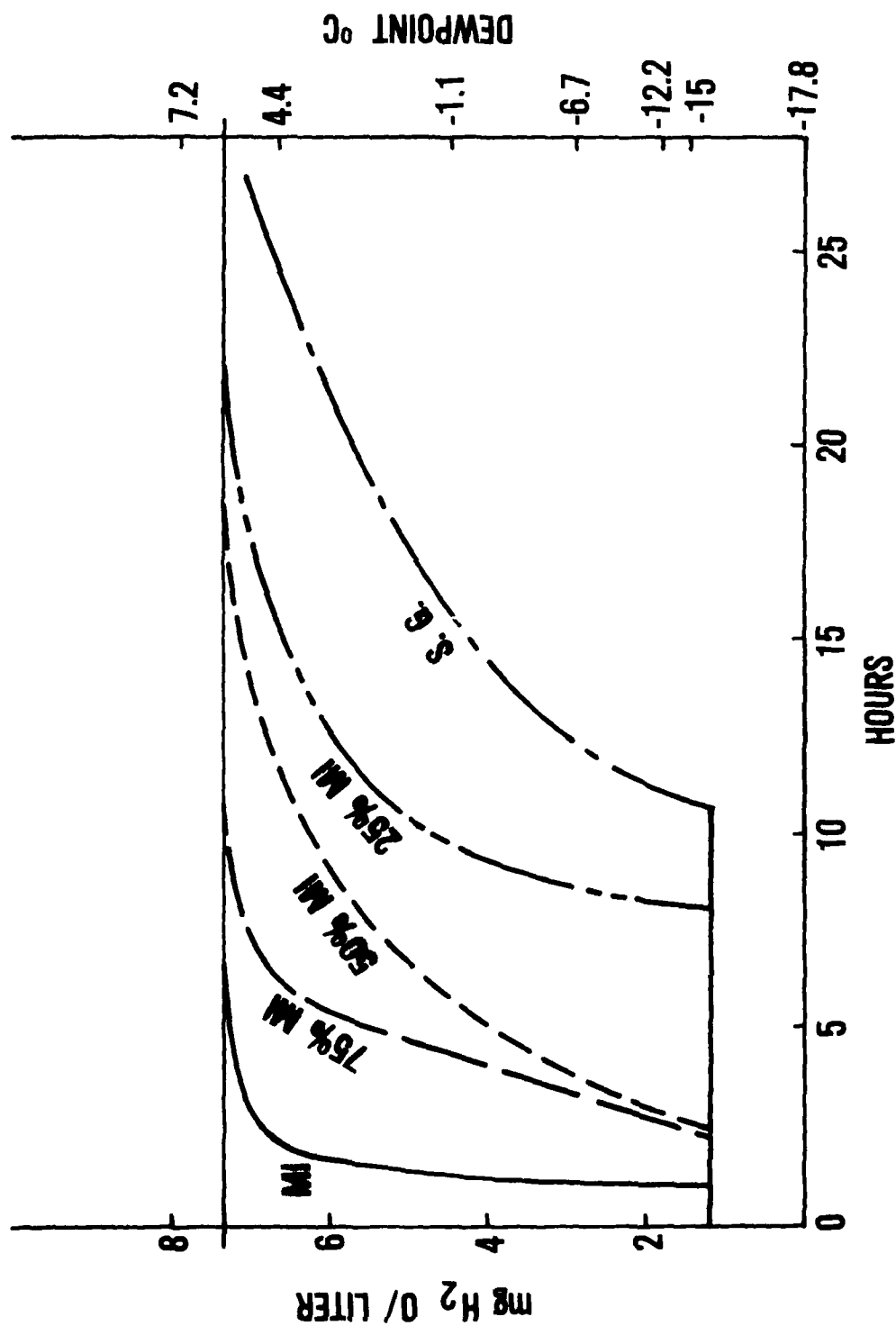


Figure 2B. Moisture breakthrough curves, RH 20 : MI charcoal/silica gel mixtures.

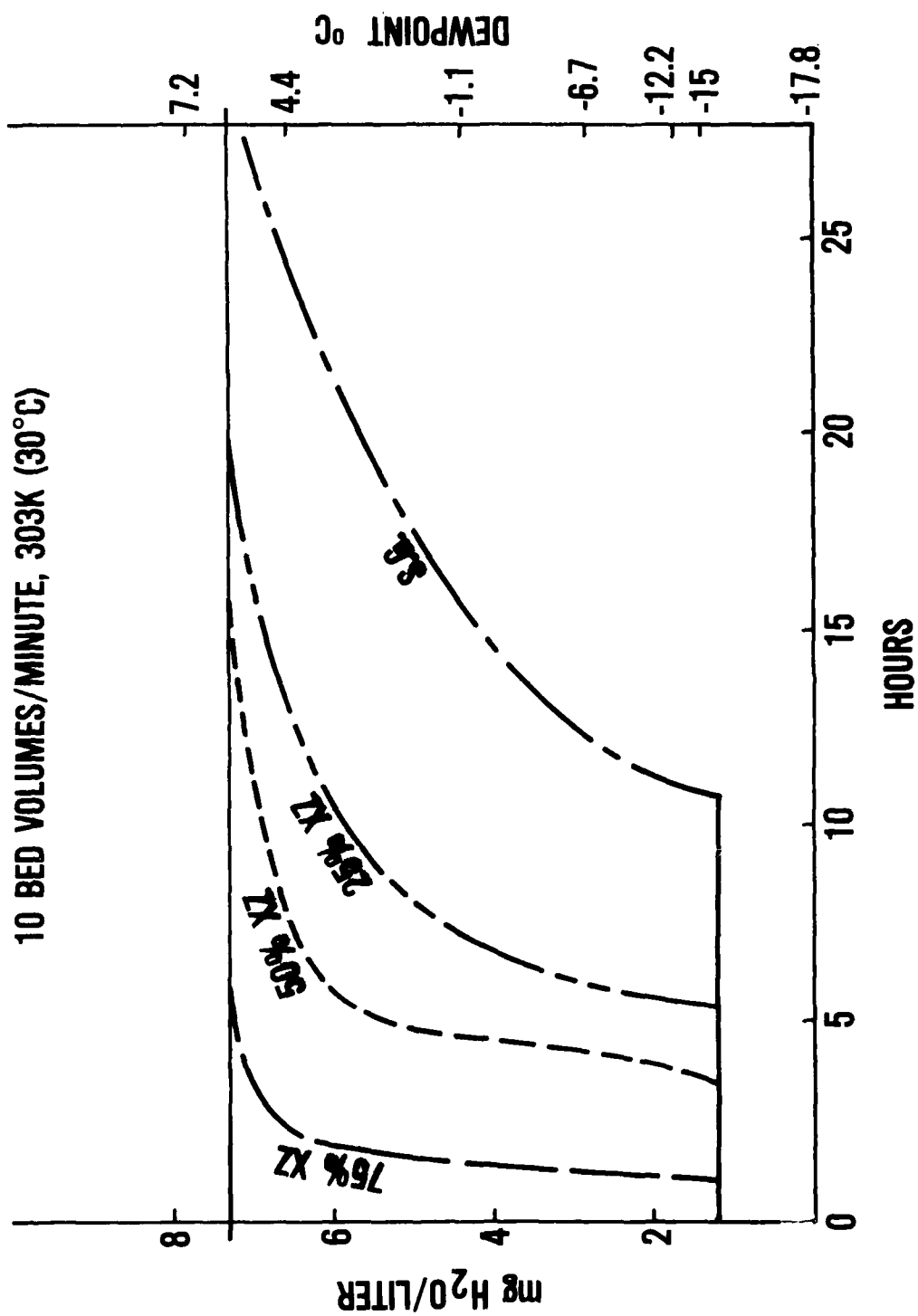


Figure 2C. Moisture breakthrough curves, RH 20%: XZ charcoal coprecipitated with silica gel.

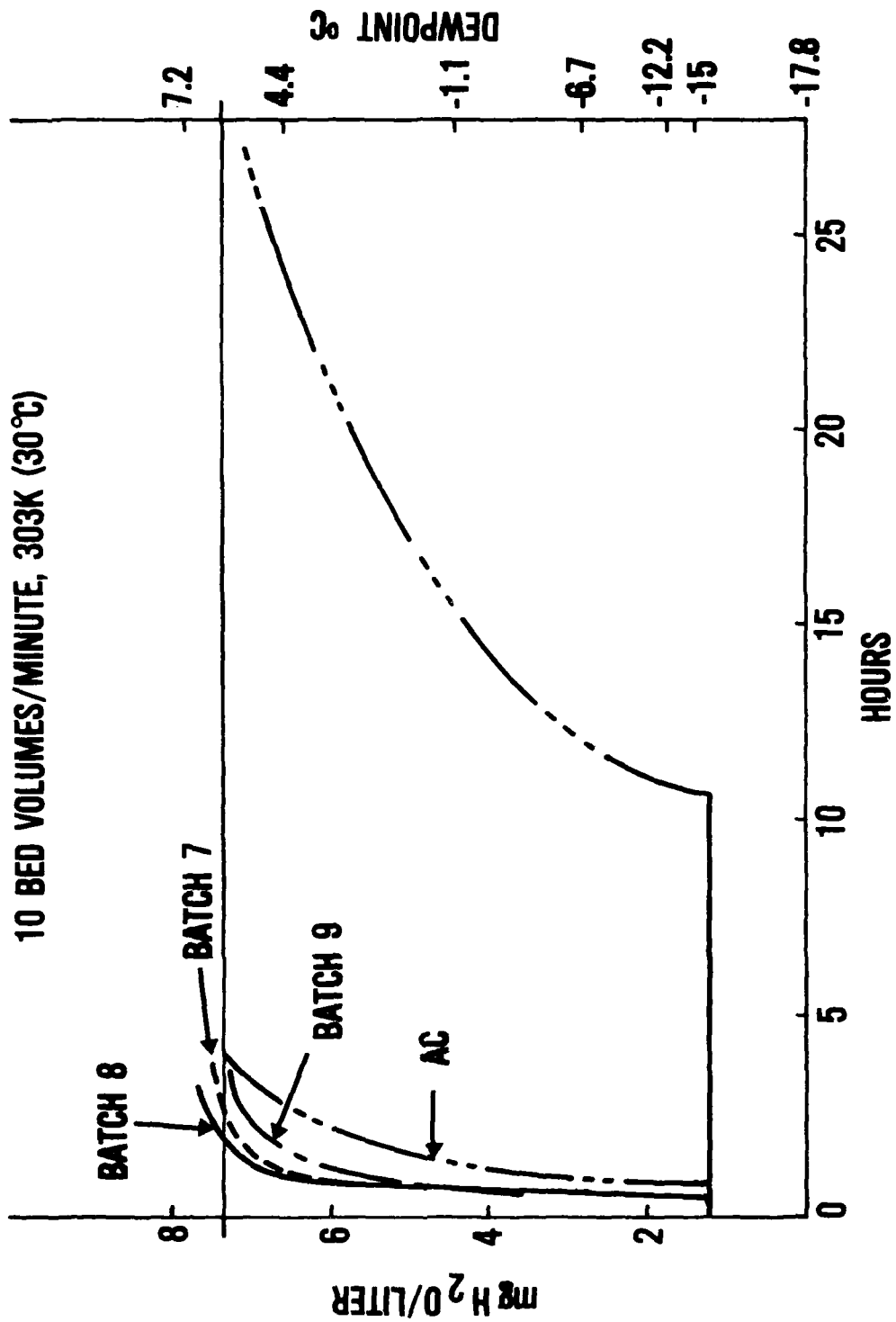


Figure 2D. Moisture breakthrough curves, RH 20 : silica-gel-coated AC charcoal.

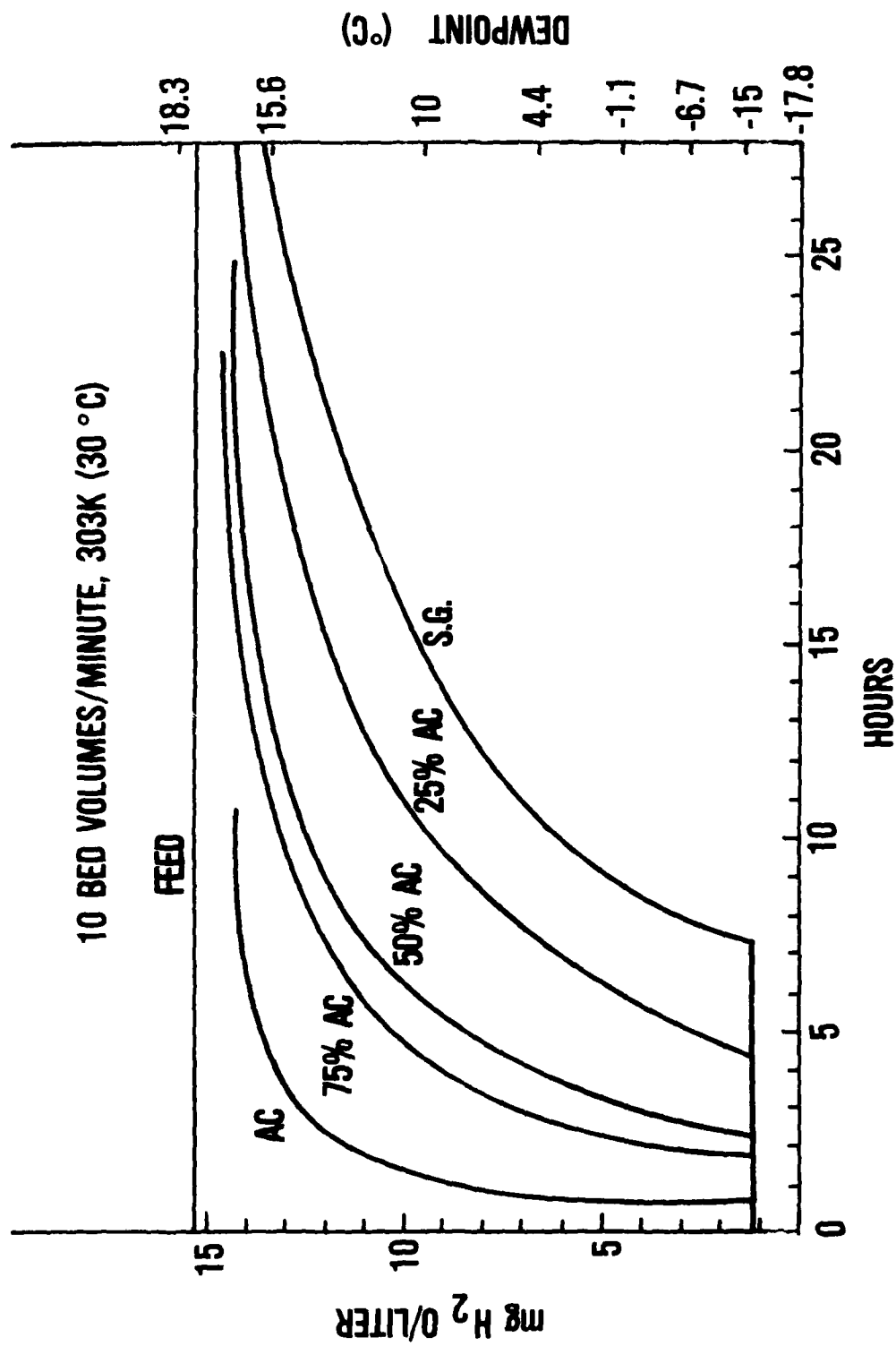


Figure 3A. Moisture breakthrough curves, RH 50%: AC charcoal/silica gel mixtures.

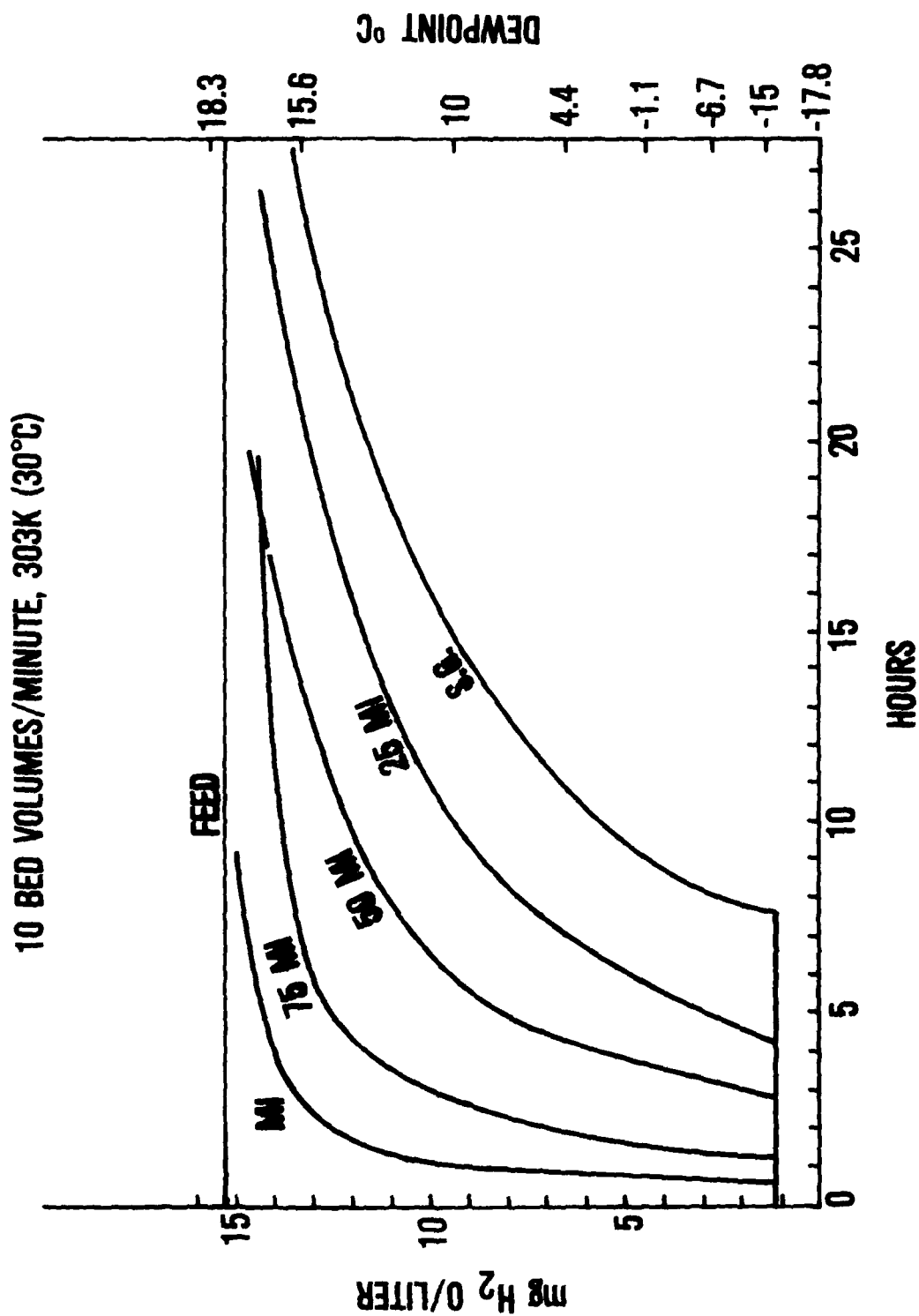


Figure 3B. Moisture breakthrough curves, RH 50 : MI charcoal/silica gel mixtures.

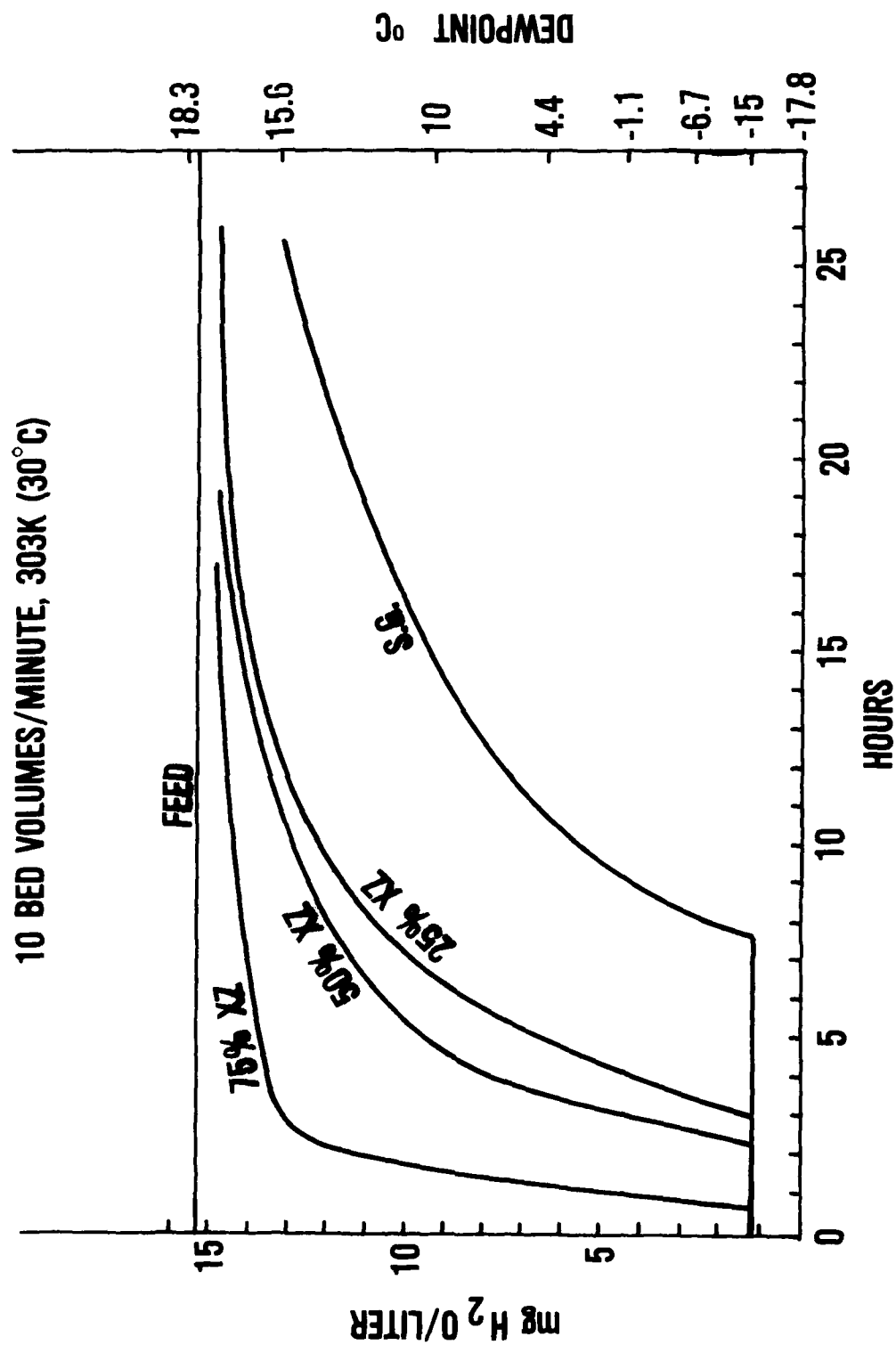


Figure 3C. Moisture breakthrough curves, RH 50%; XZ charcoal coprecipitated with silica gel.

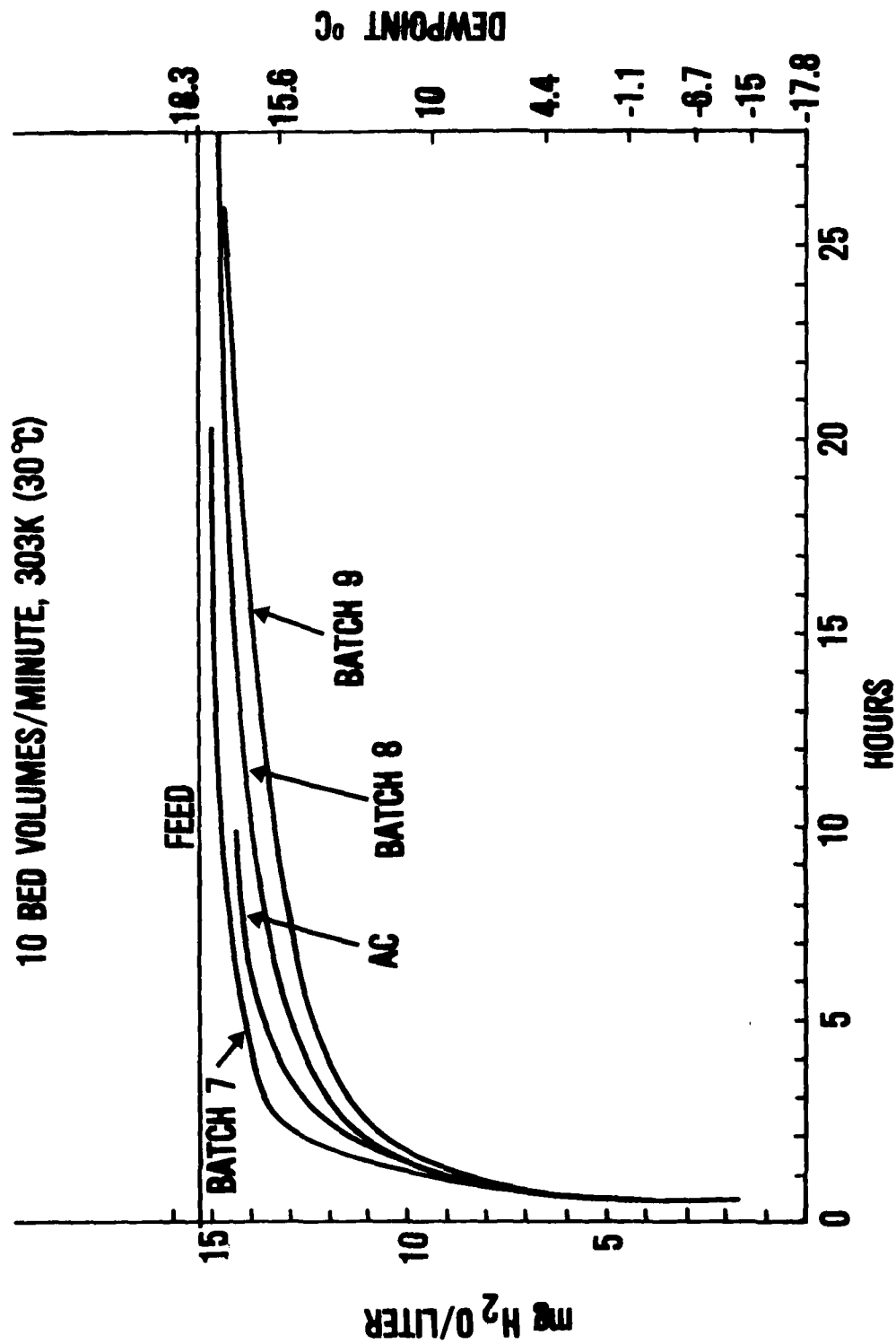


Figure 3D. Moisture breakthrough curves. RH 50 : silica-gel-coated AC charcoal.



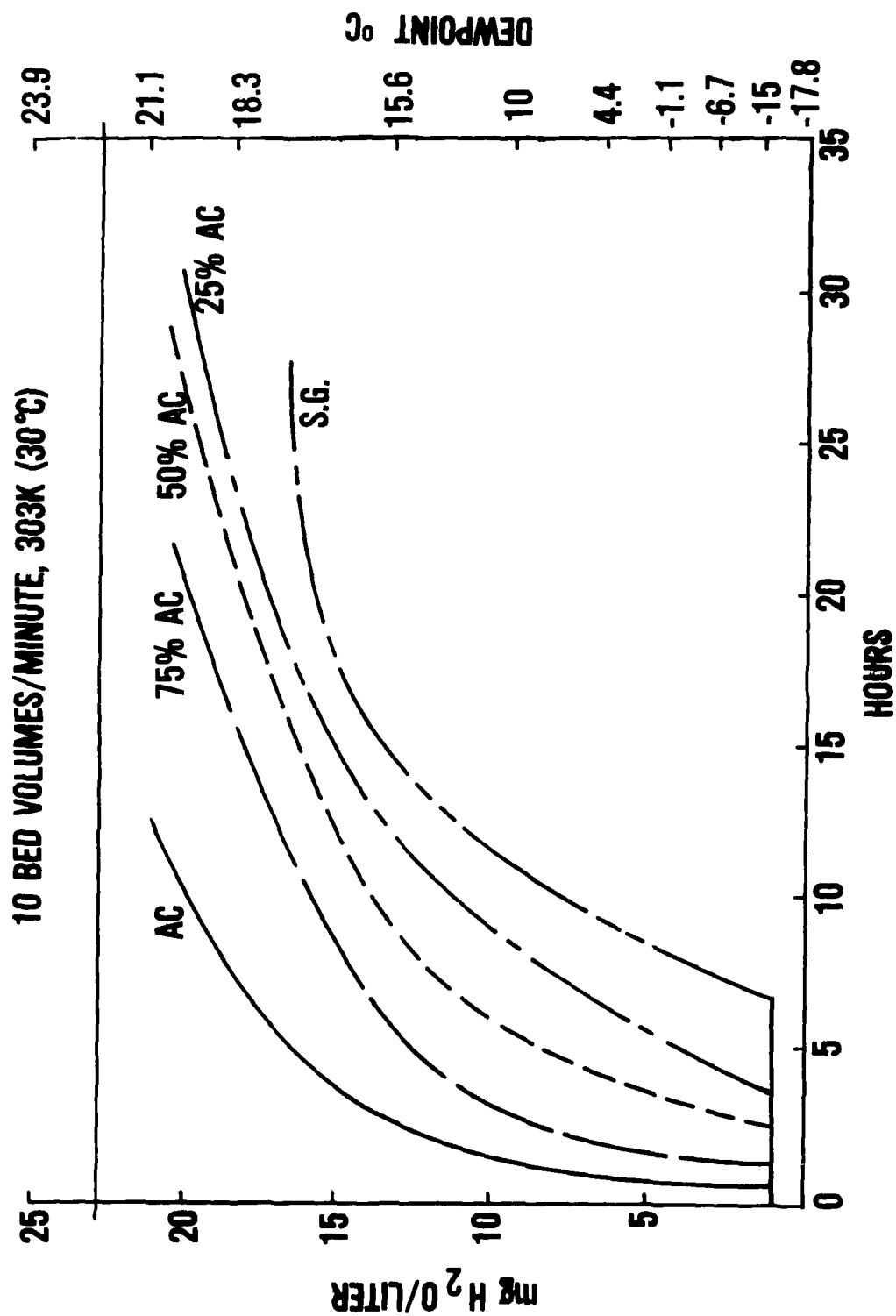


Figure 4A. Moisture breakthrough curves. RH 75%; AC charcoal/silica gel mixtures.

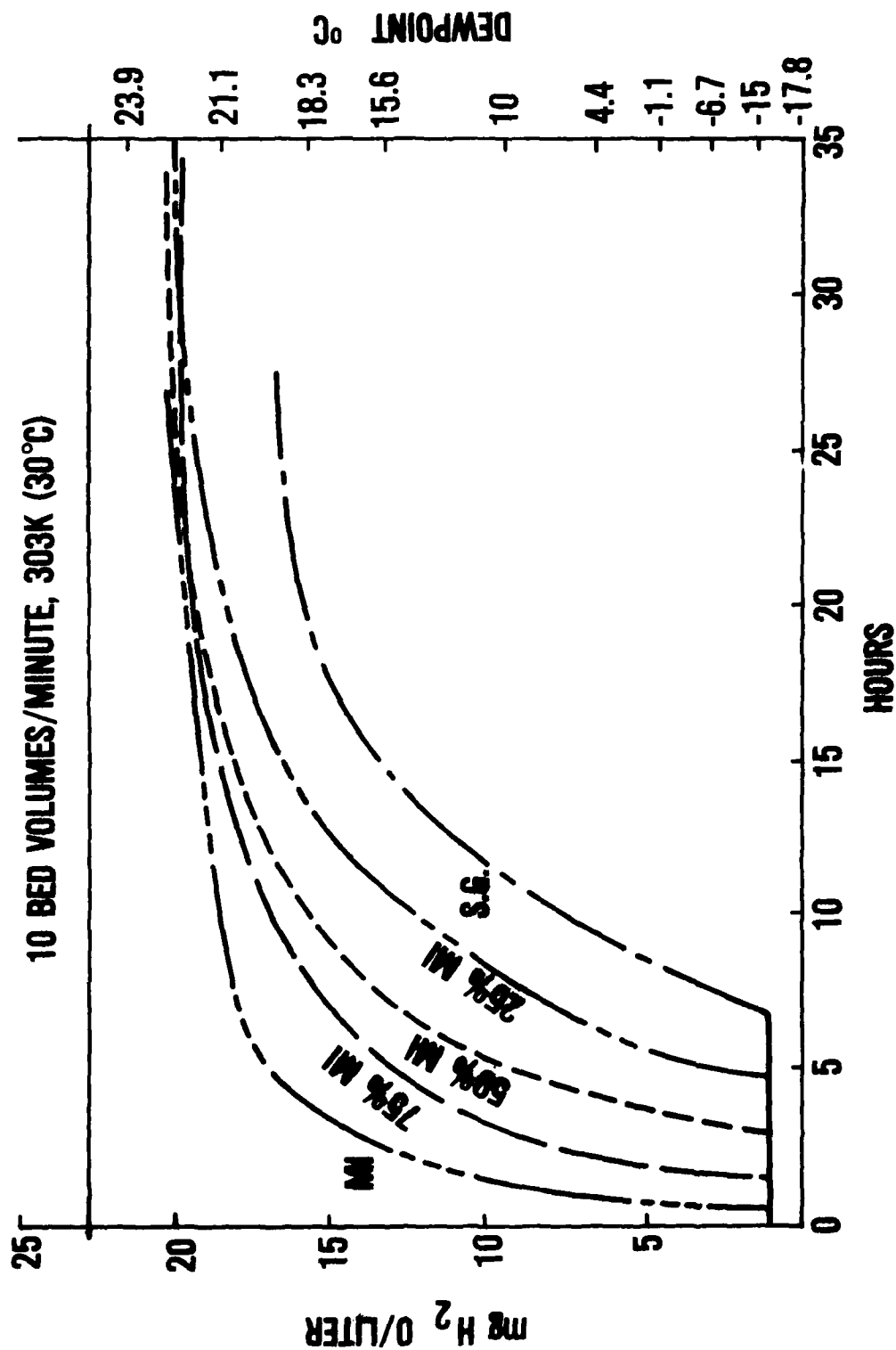


Figure 4B. Moisture breakthrough curves. RH 75 : MI charcoal/silica gel mixtures.

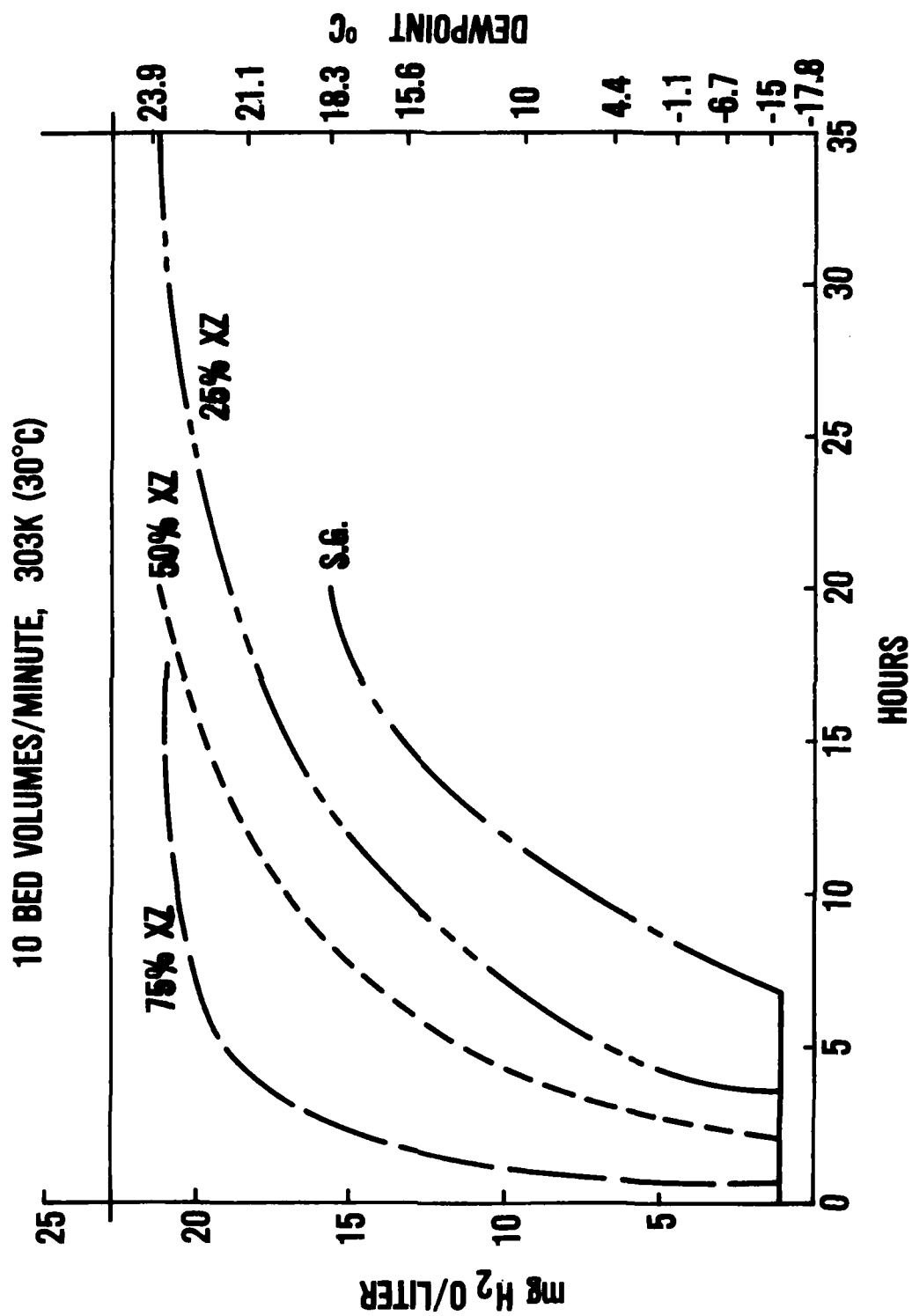


Figure 4C. Moisture breakthrough curves, RH 75%: XZ coprecipitated with silica gel.

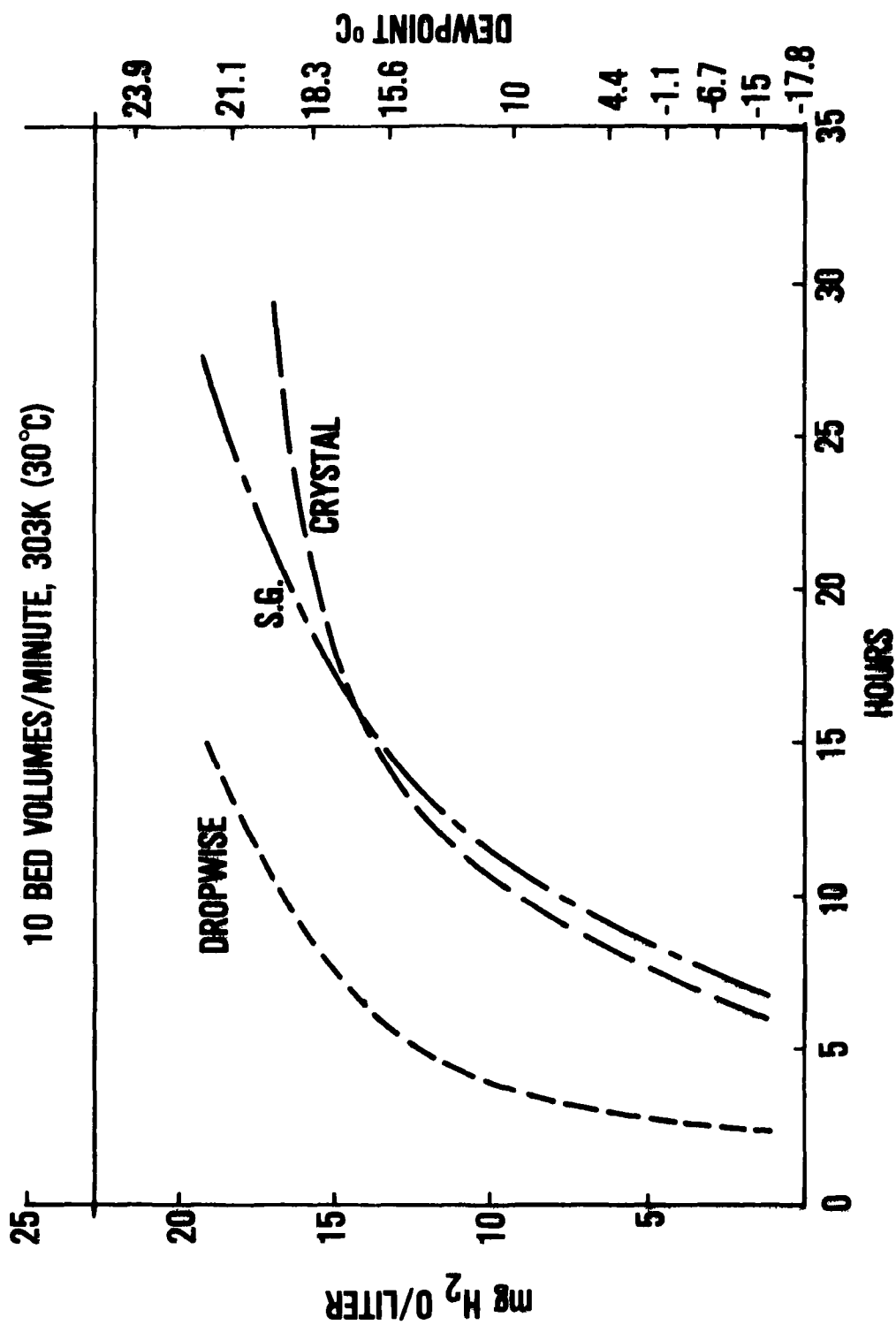


Figure 4D. Moisture breakthrough curves. RH 75 : silica gels.

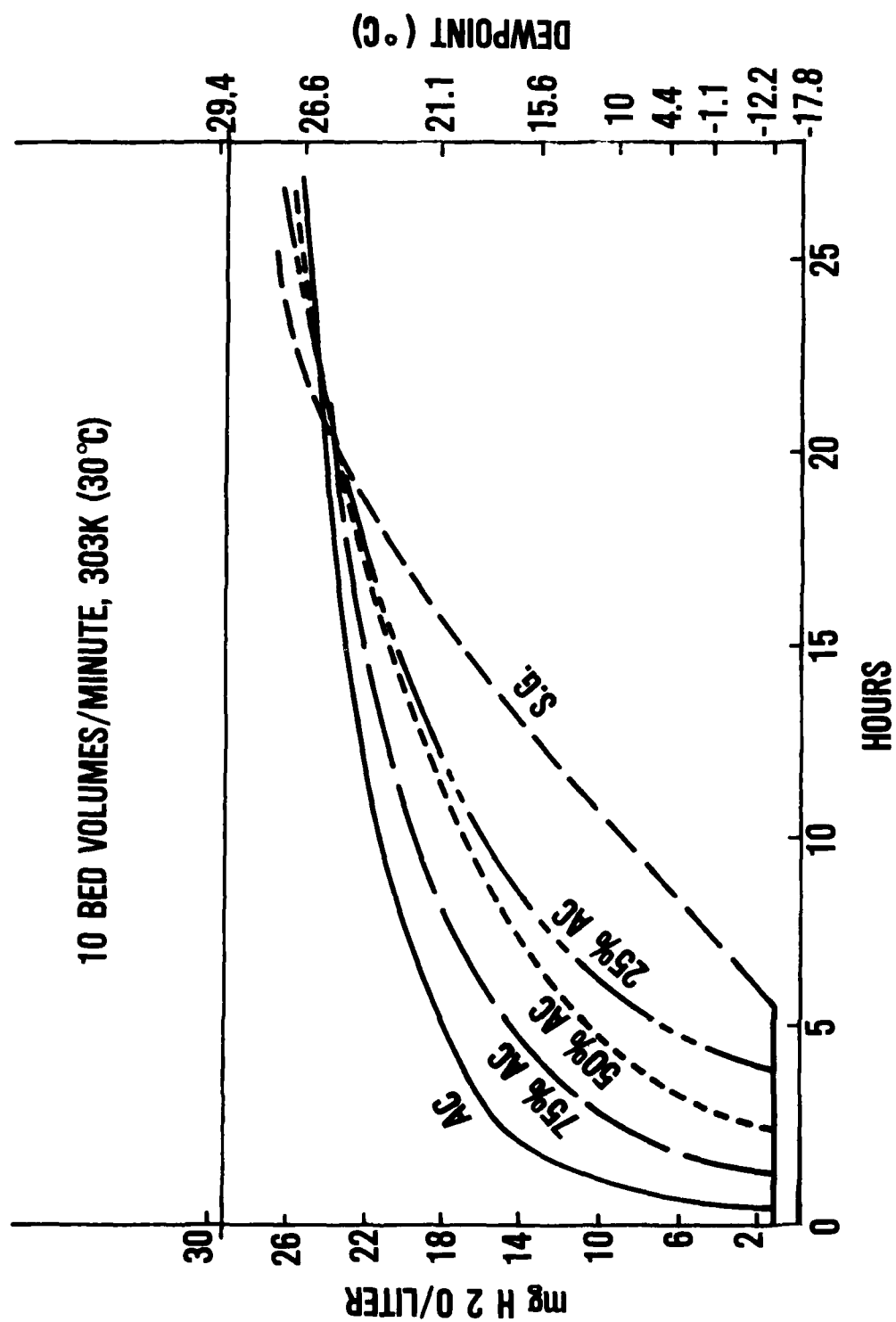


Figure 5A. Moisture breakthrough curves. RH 95%: AC charcoal/silica gel mixtures.

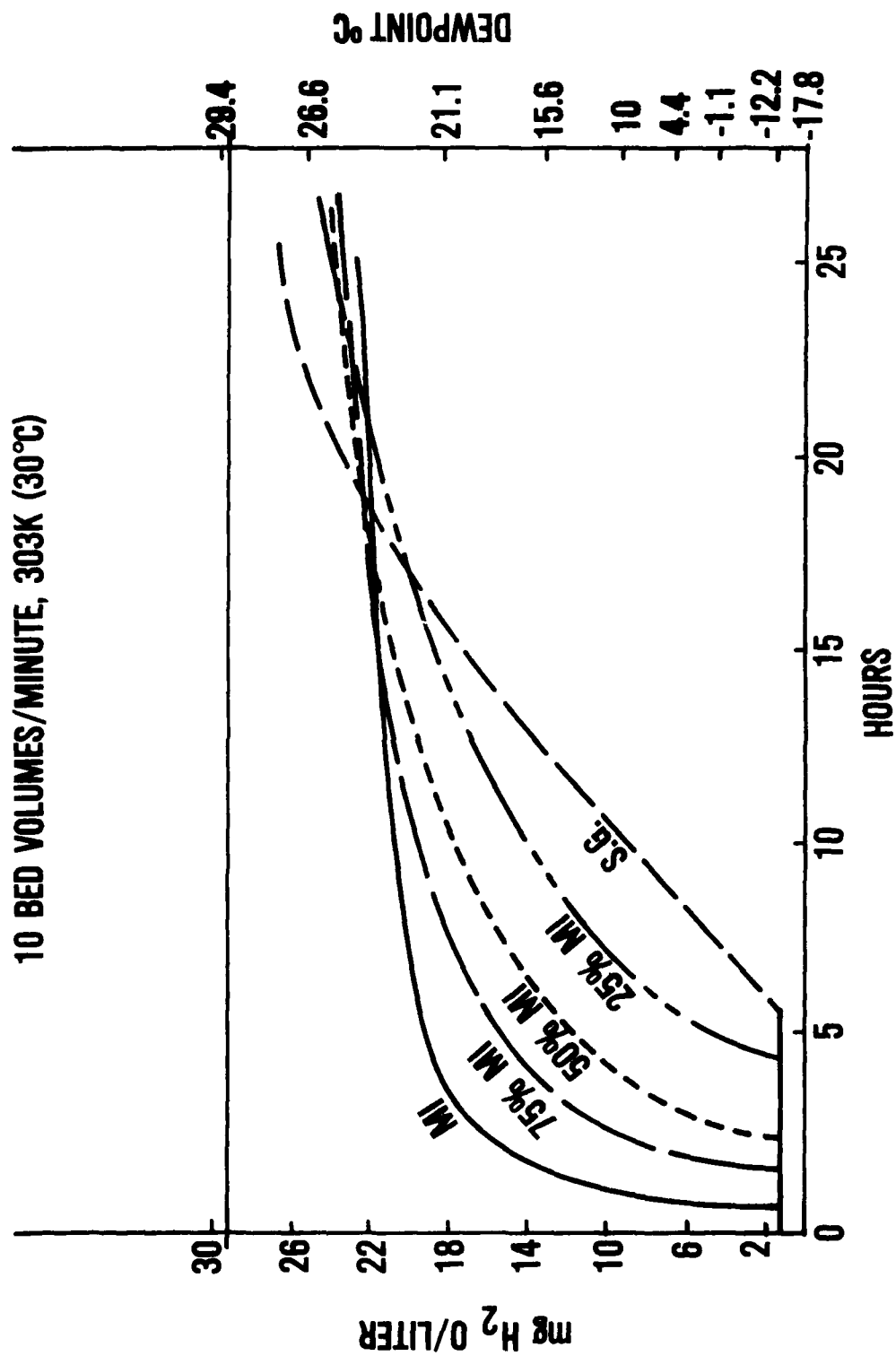


Figure 5B. Moisture breakthrough curves, RH 95: MI charcoal/silica gel mixtures.

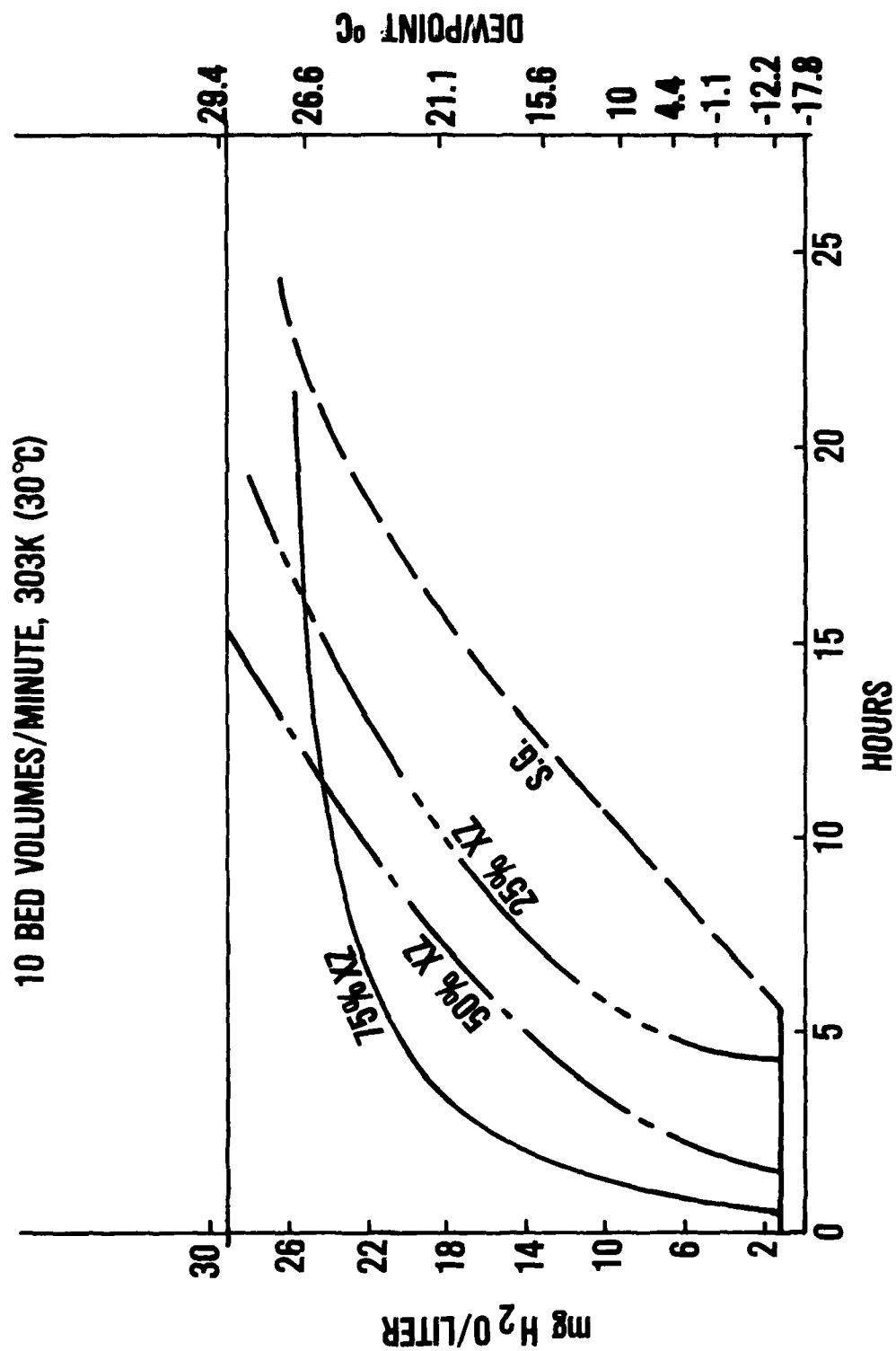


Figure 5C. Moisture breakthrough curves, RH 95%: XZ coprecipitated with silica gel.

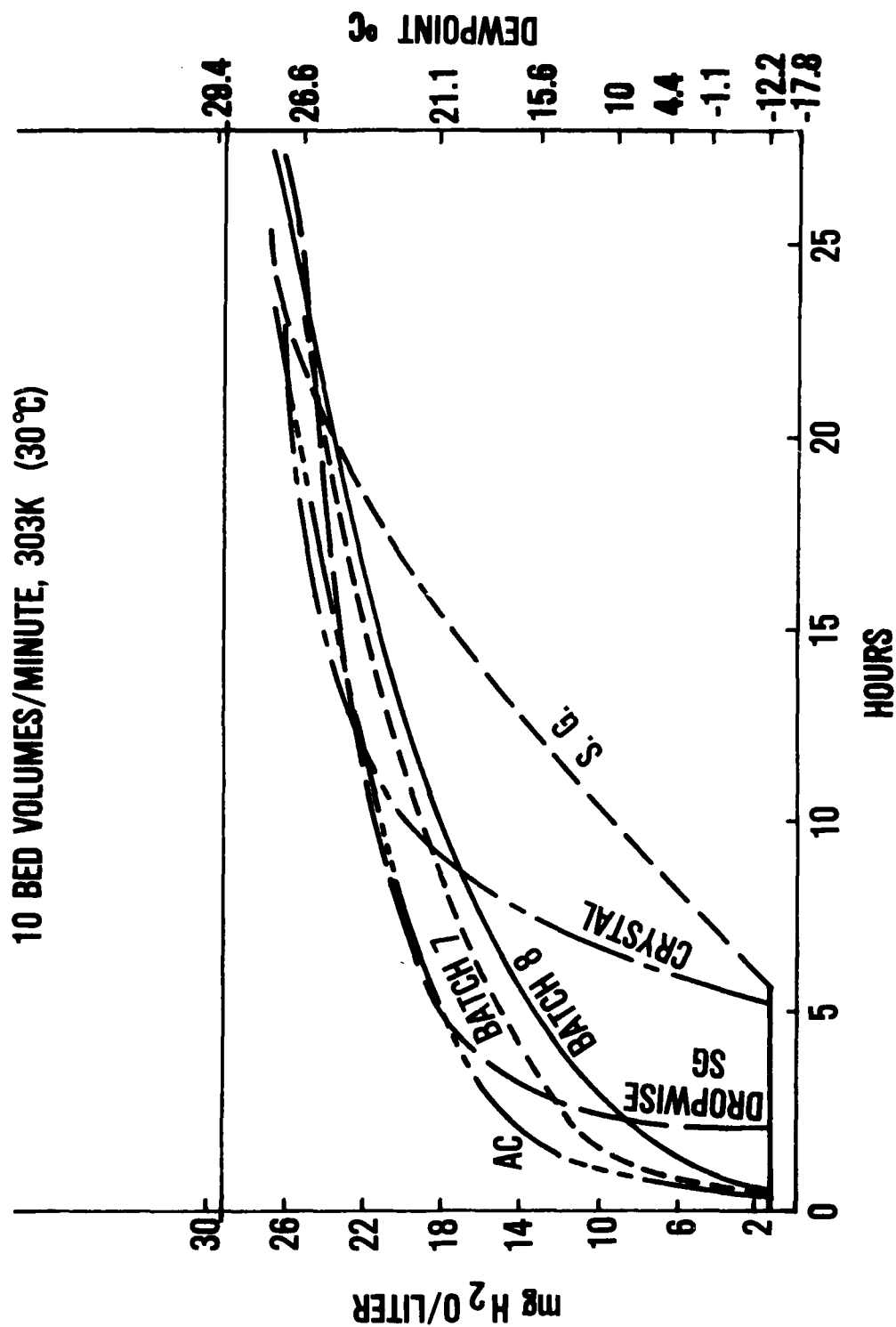


Figure 5D. Moisture breakthrough curves. RH 95%: silica-gel-coated AC charcoal and silica gels.



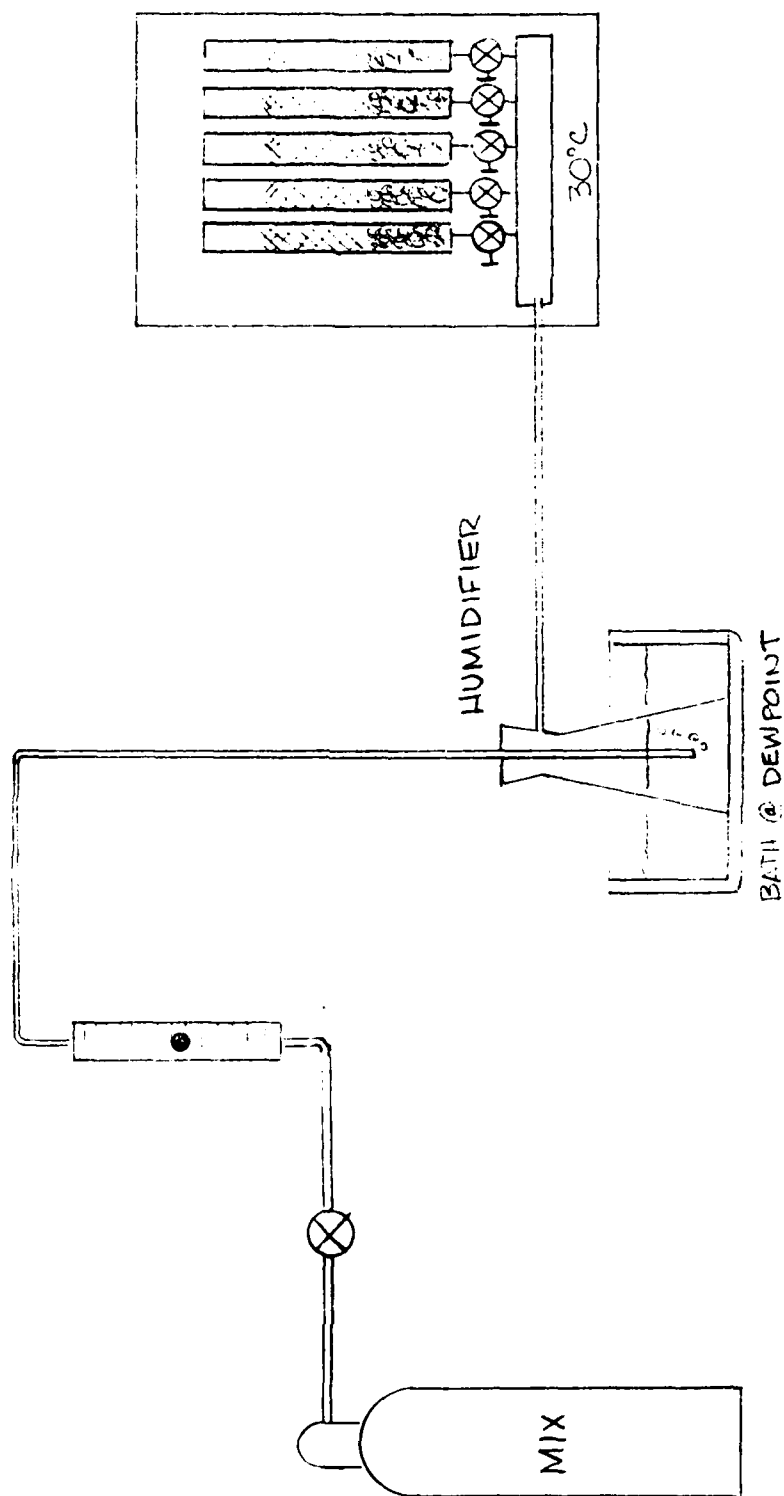


Figure 6. Organic vapor test apparatus.

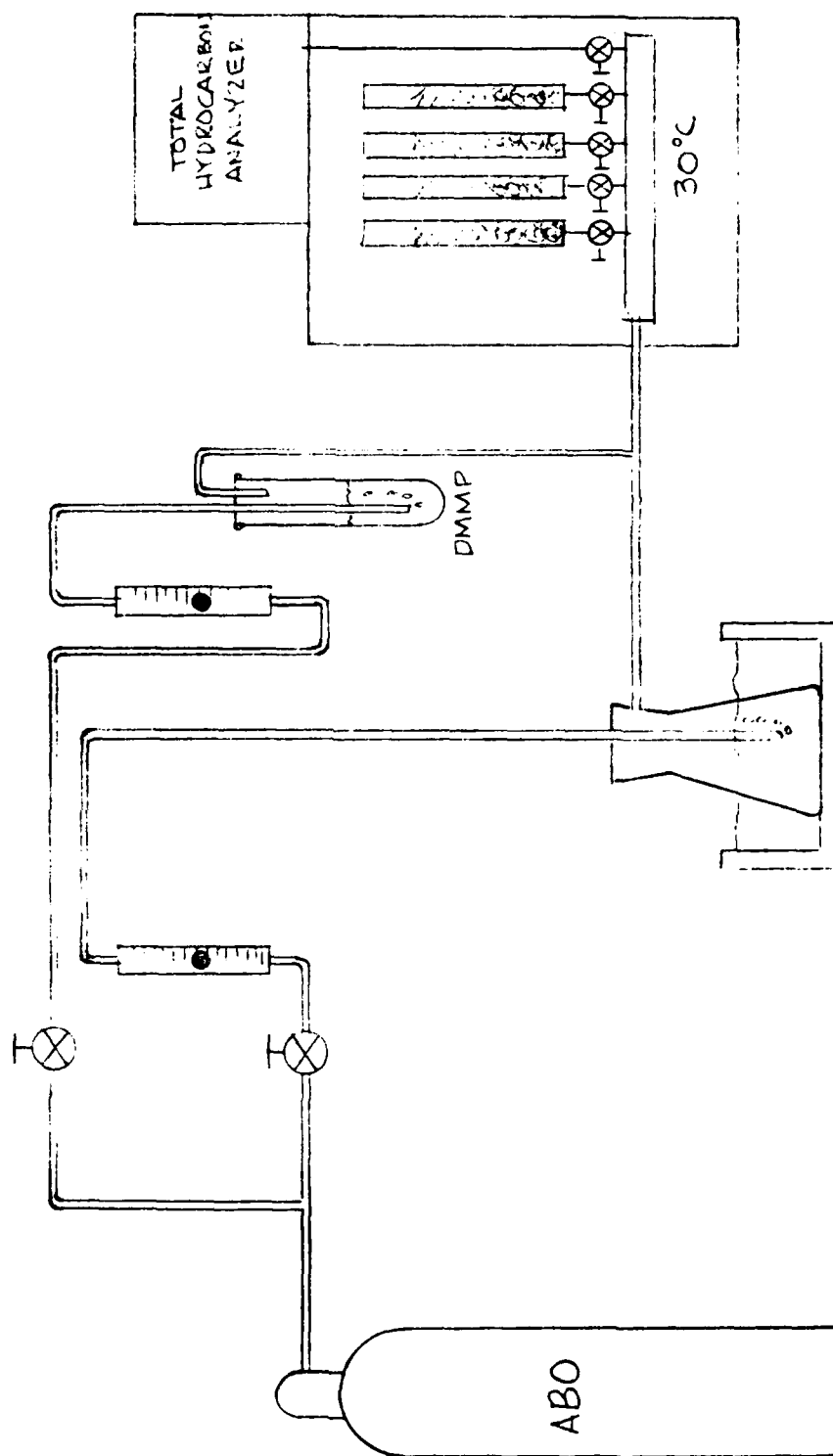


Figure 7. Test apparatus used for dimethyl methylphosphonate.

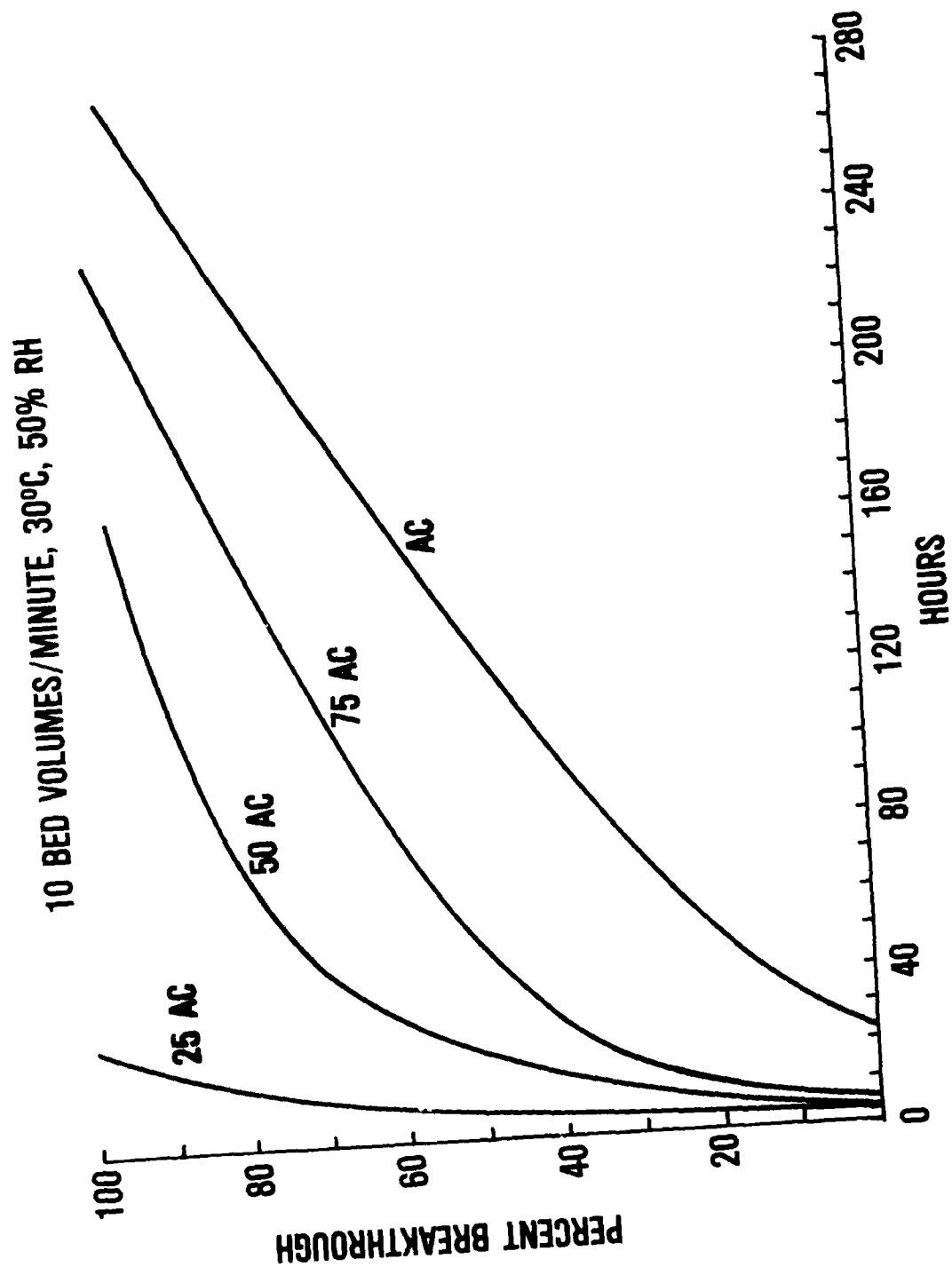


Figure 8A. Acetaldehyde breakthrough (100 ppm): AC charcoal/silica gel mixtures.

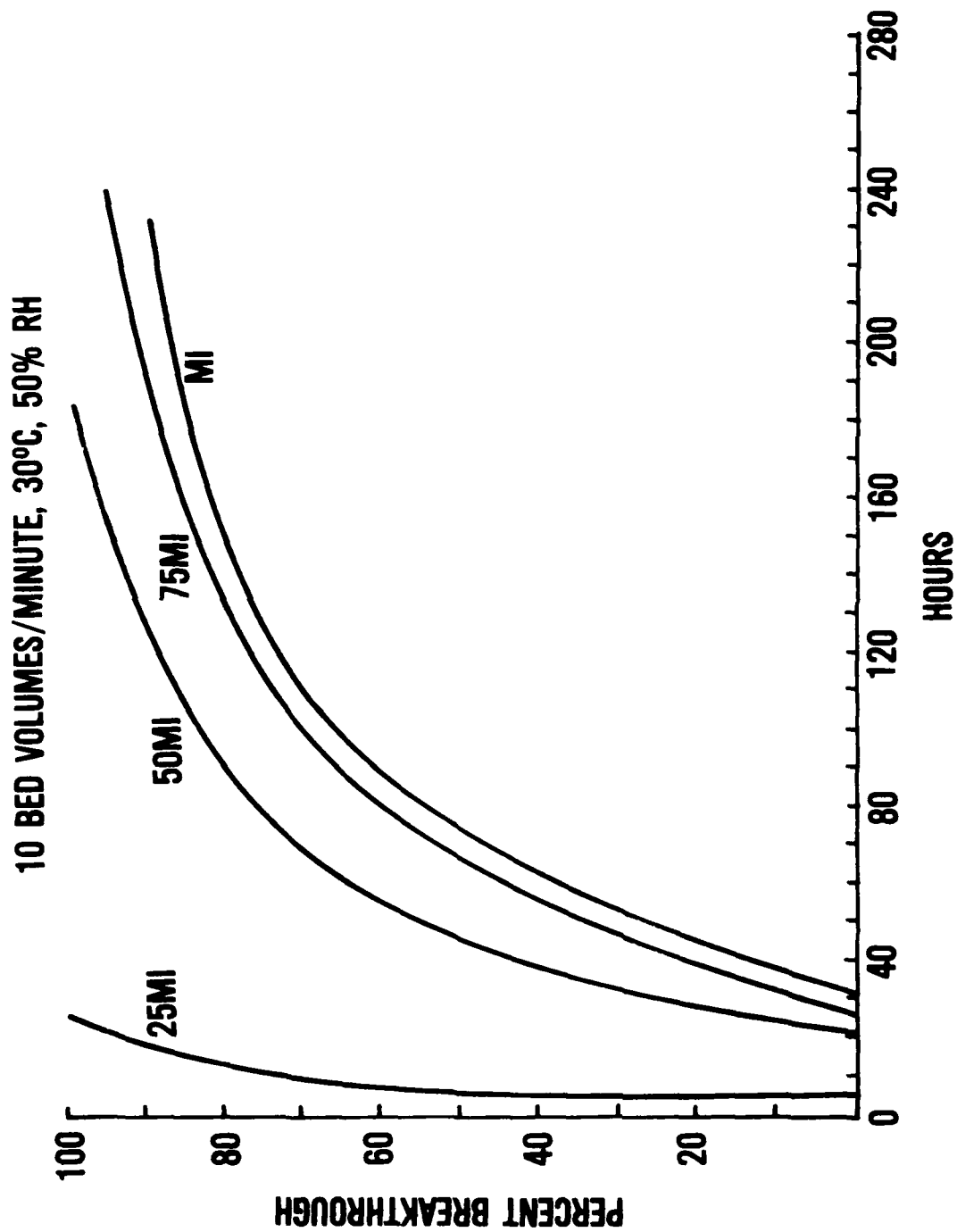


Figure 8B. Acetaldehyde breakthrough (100 ppm): MI charcoal/silica gel mixtures.

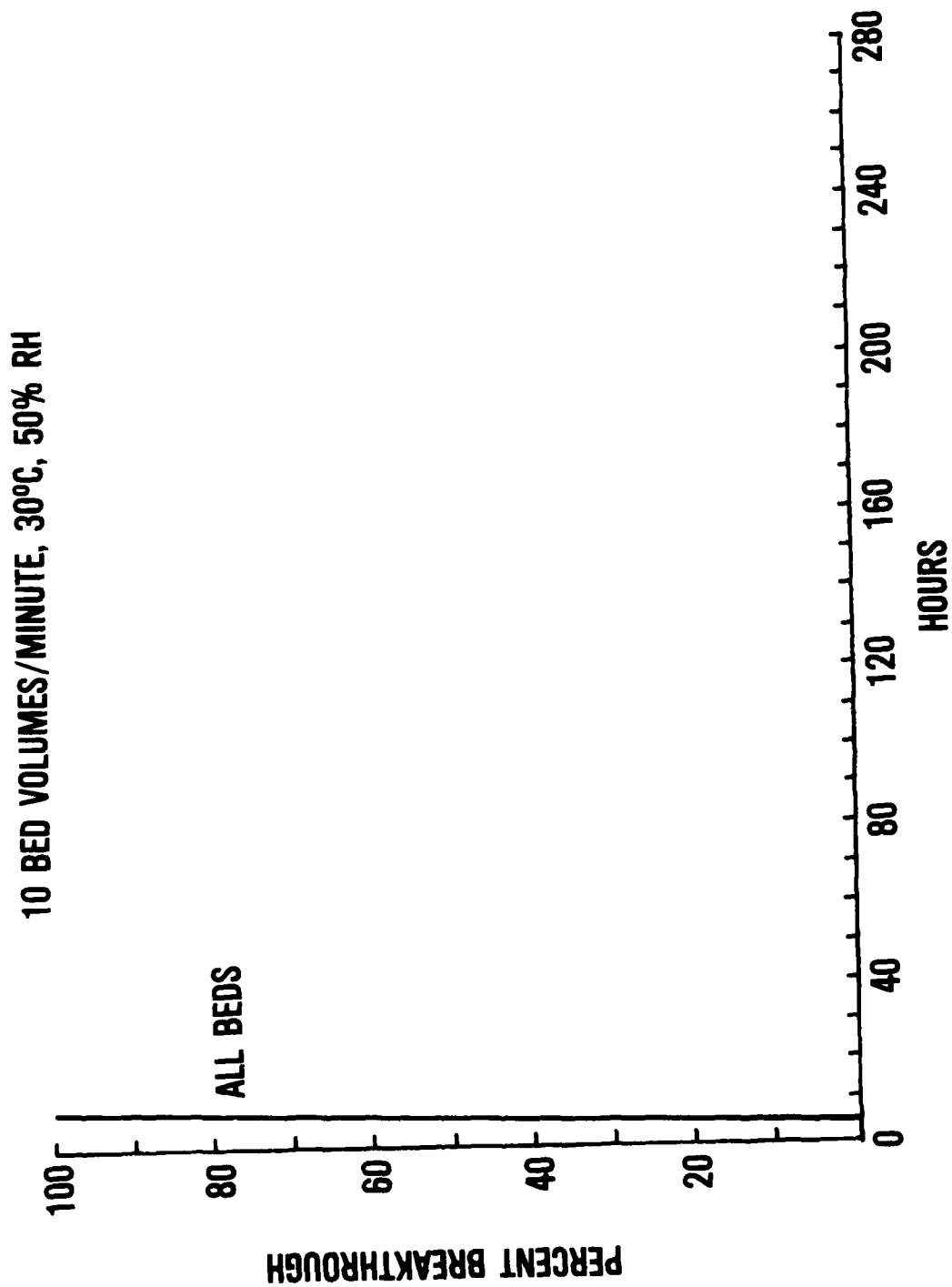


Figure 8C. Acetaldehyde breakthrough (100 ppm): XZ charcoal coprecipitated with silica gel.

10 BED VOLUMES/MINUTE, 30°C, 50% RH

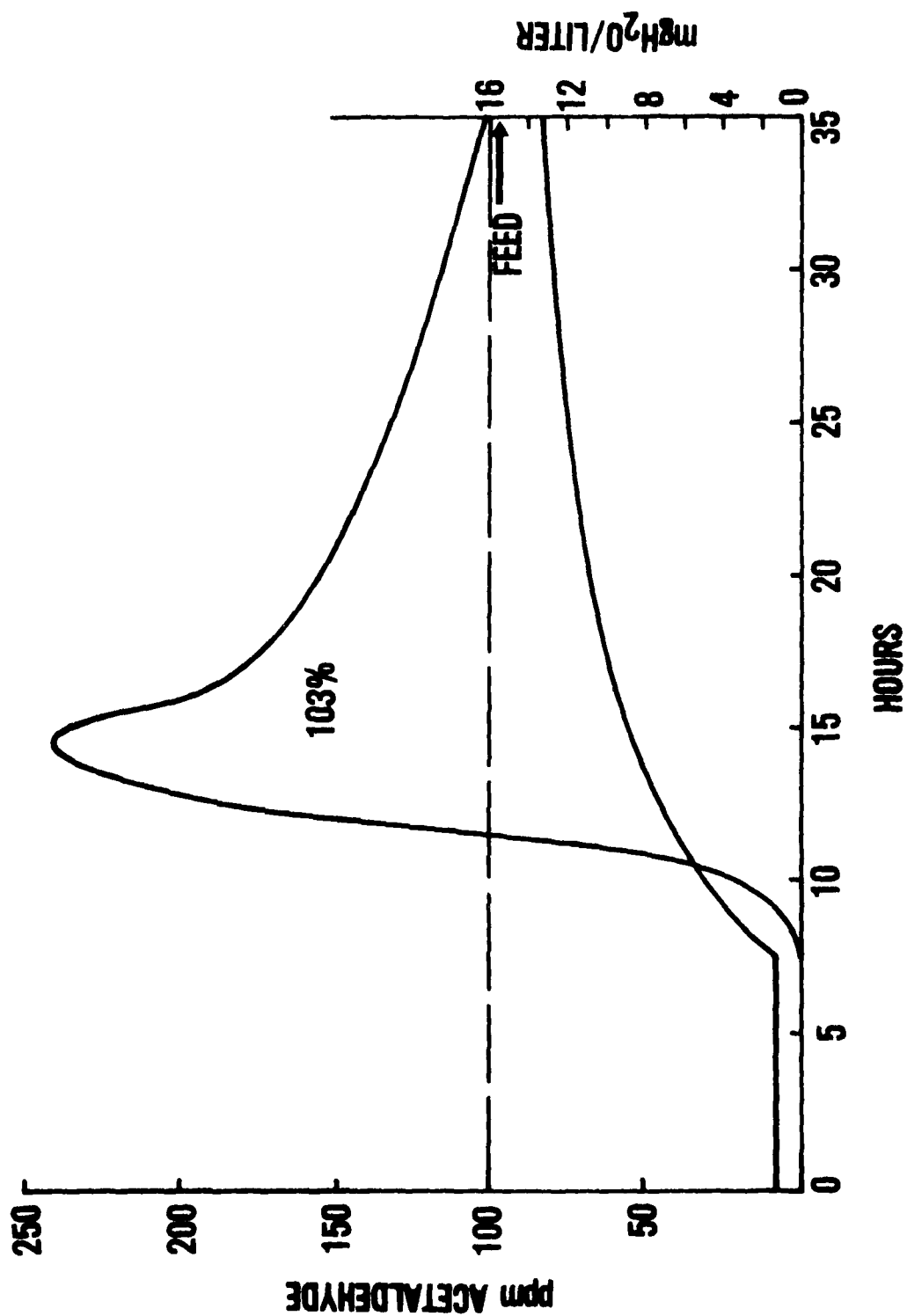


Figure 8D. Acetaldehyde breakthrough (100 ppm): silica gel.

10 BED VOLUMES/MINUTE, 30°C, 50% RH

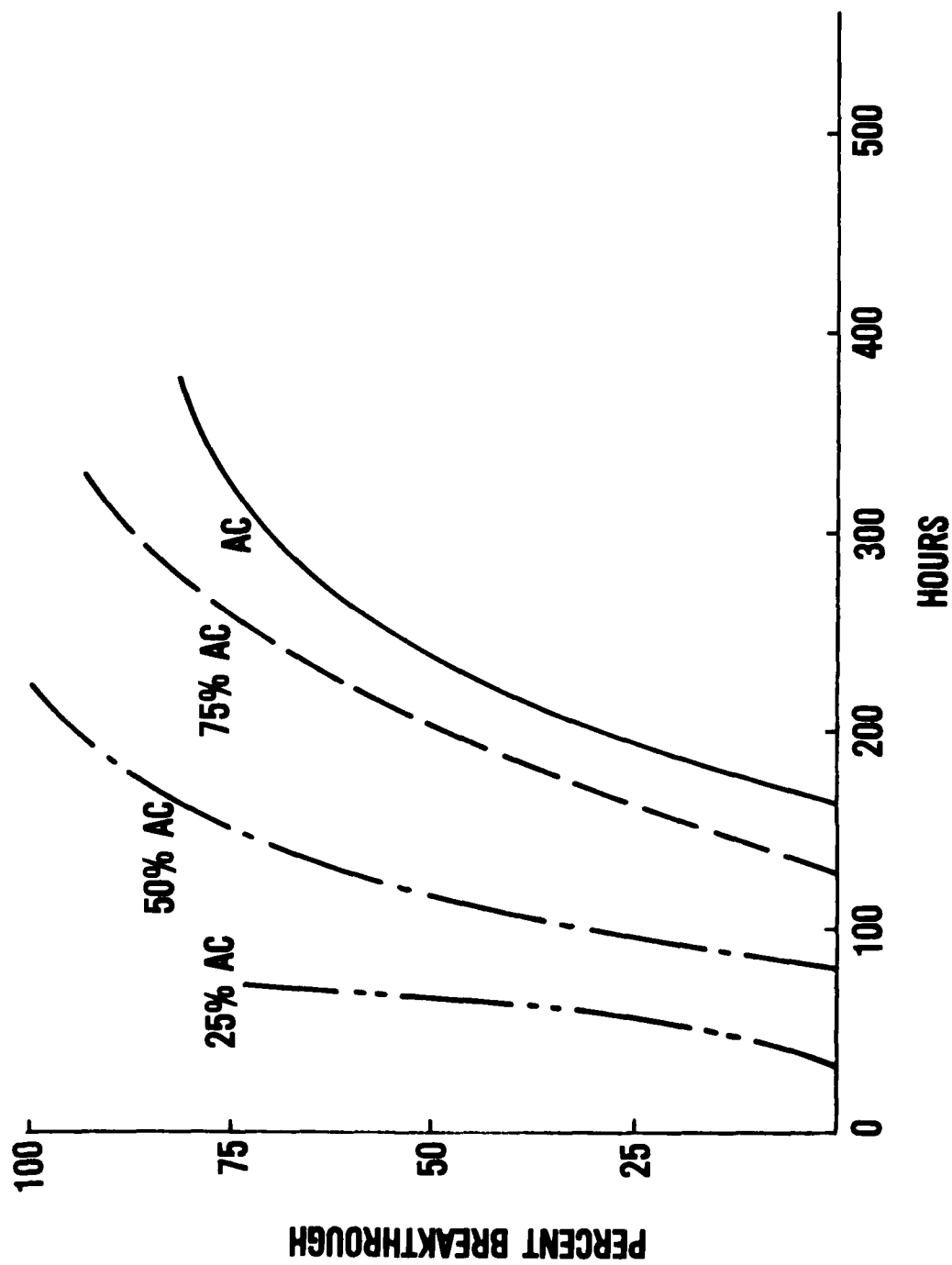


Figure 9A. Acrolein breakthrough (100 ppm): AC charcoal/silica gel mixtures.

10 BED VOLUMES/MINUTE, 30°C, 50% RH

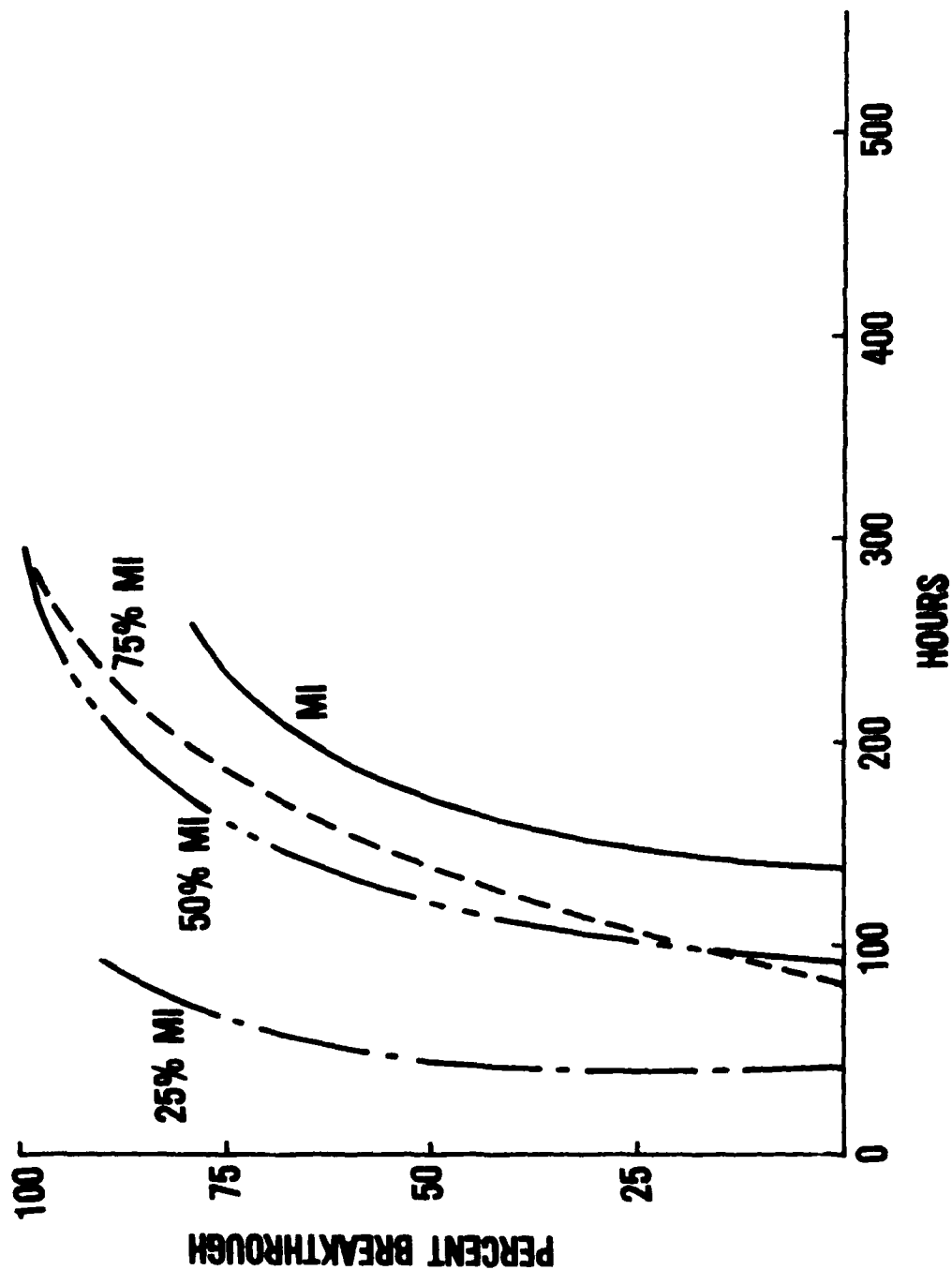


Figure 9B. Acrolein breakthrough (100 ppm): MI charcoal/silica gel mixtures.



10 BED VOLUMES/MINUTE, 30°C, 50% RH

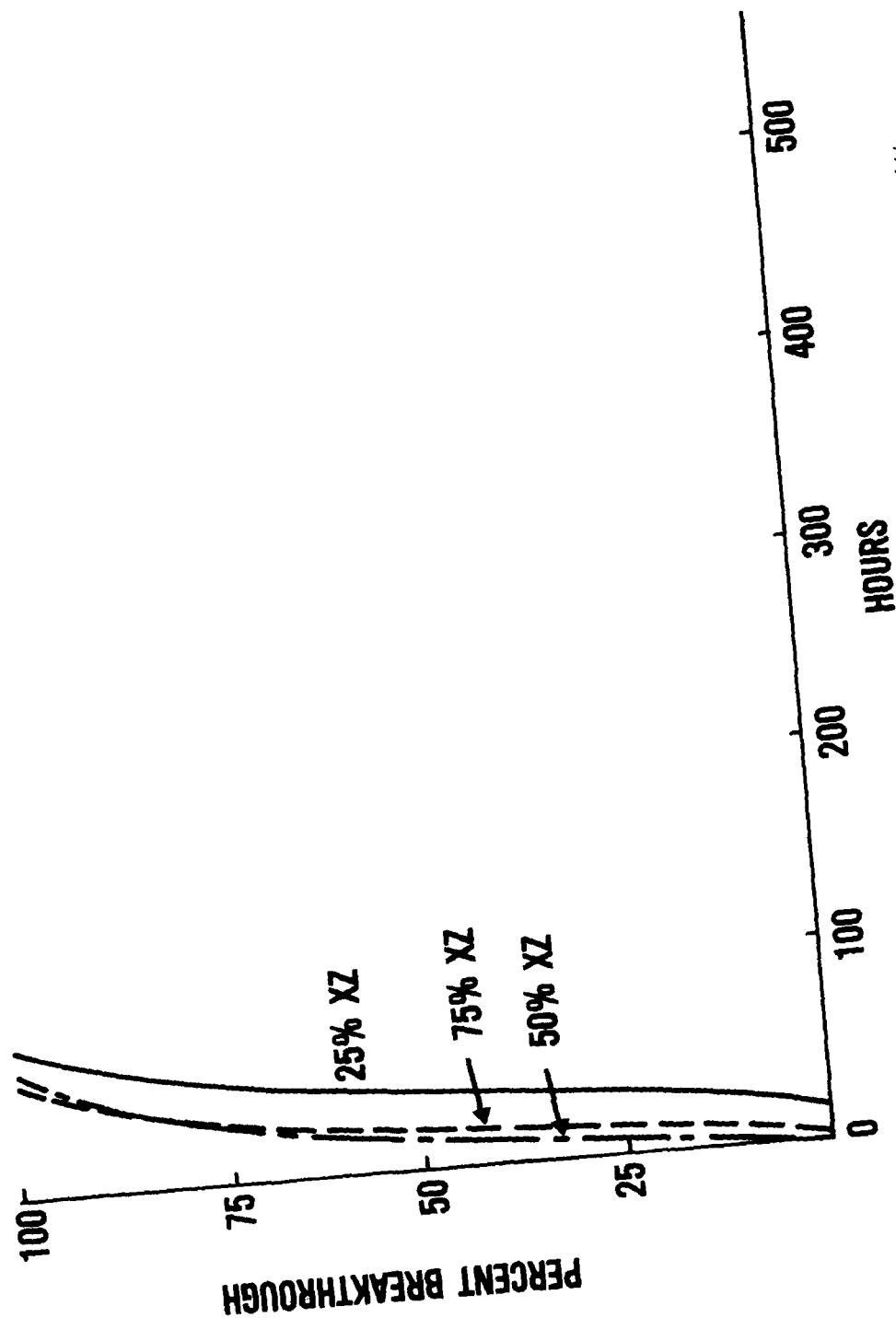


Figure 9C. Acrolein breakthrough (100 ppm): XZ charcoal coprecipitated with silica gel.

10 BED VOLUMES/MINUTE, 30°C, 50% RH

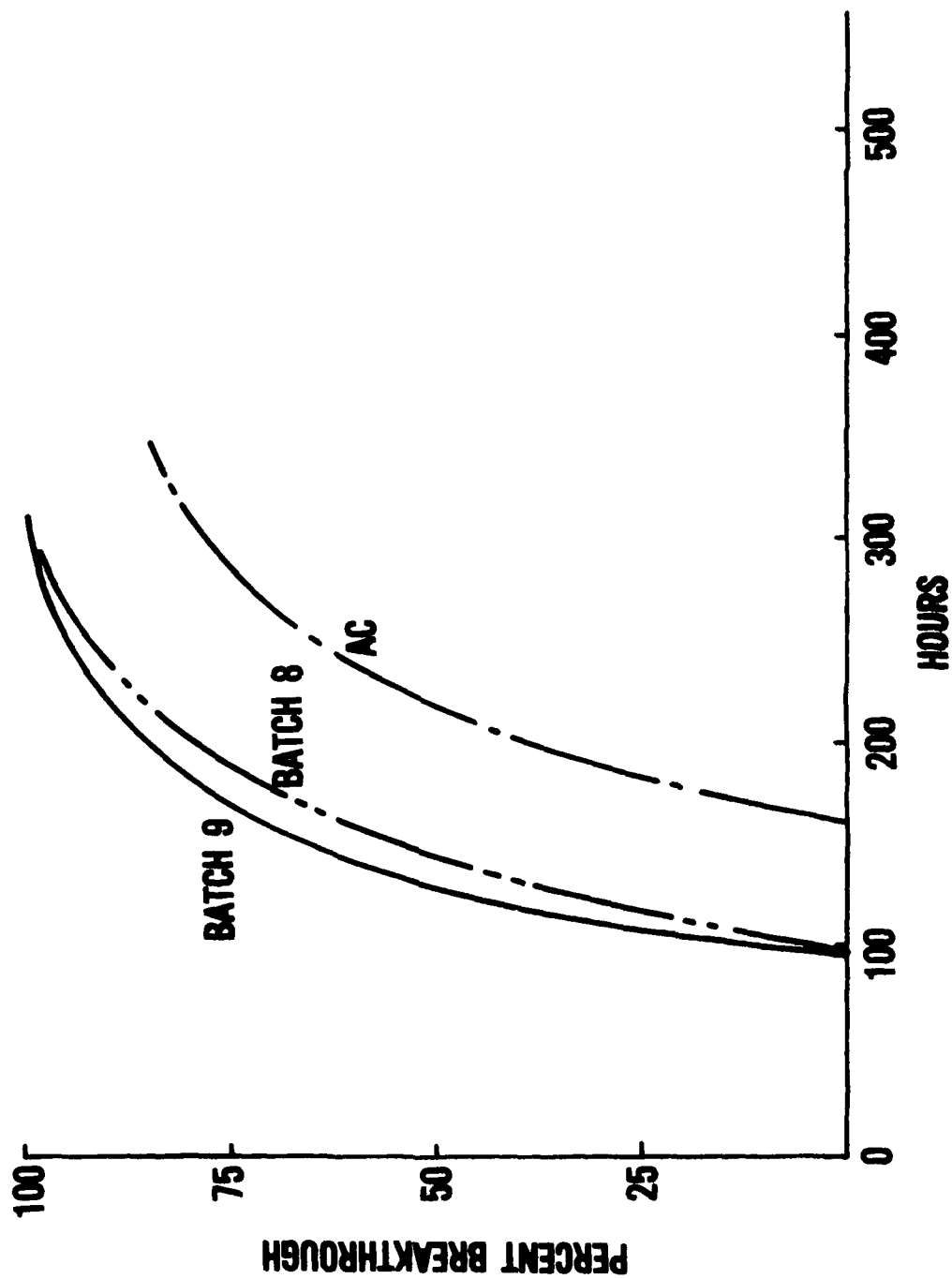


Figure 9D. Acrolein breakthrough (100 ppm): silica-gel-coated AC charcoal.

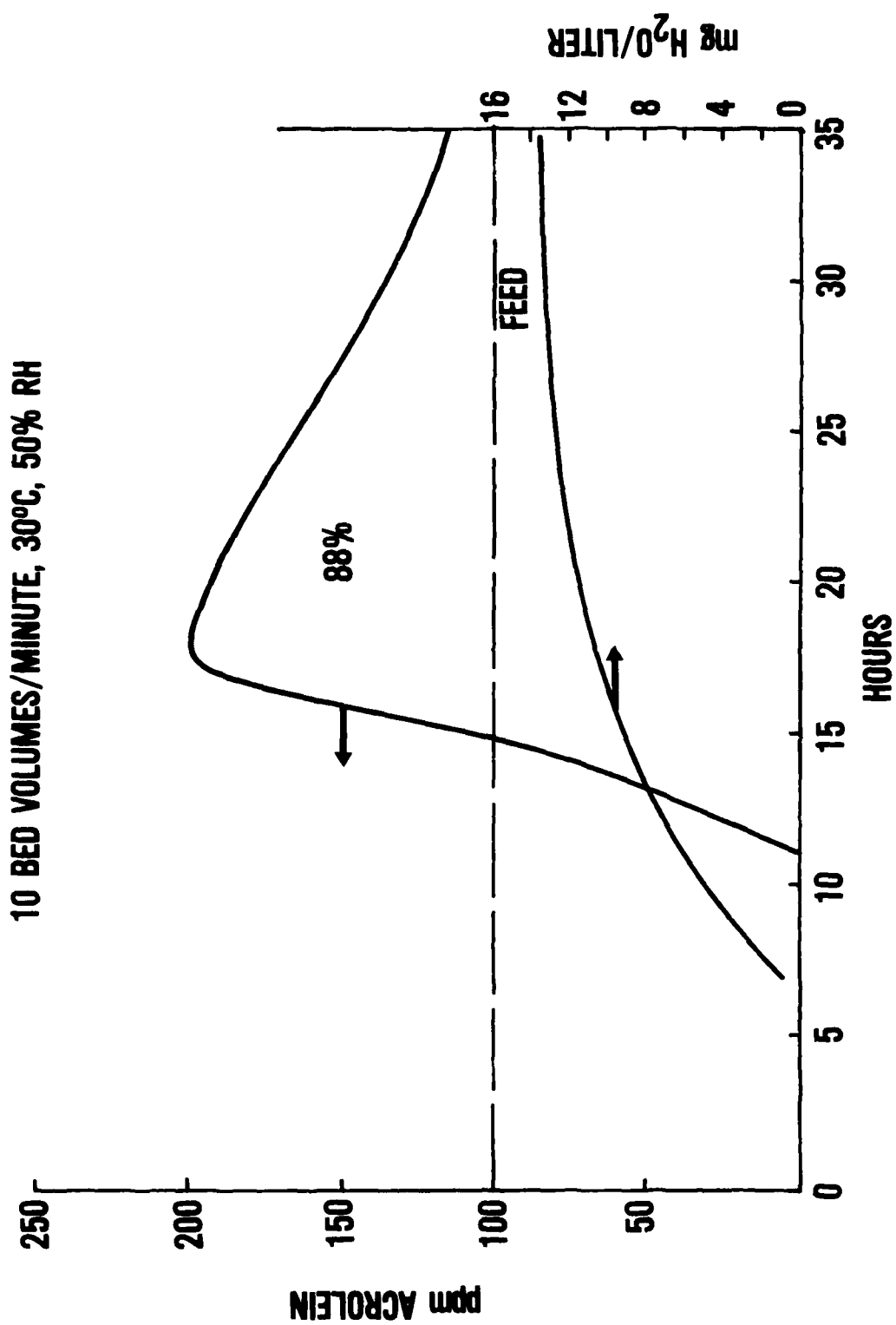


Figure 9E. Acrolein breakthrough (100 ppm): silica gel.

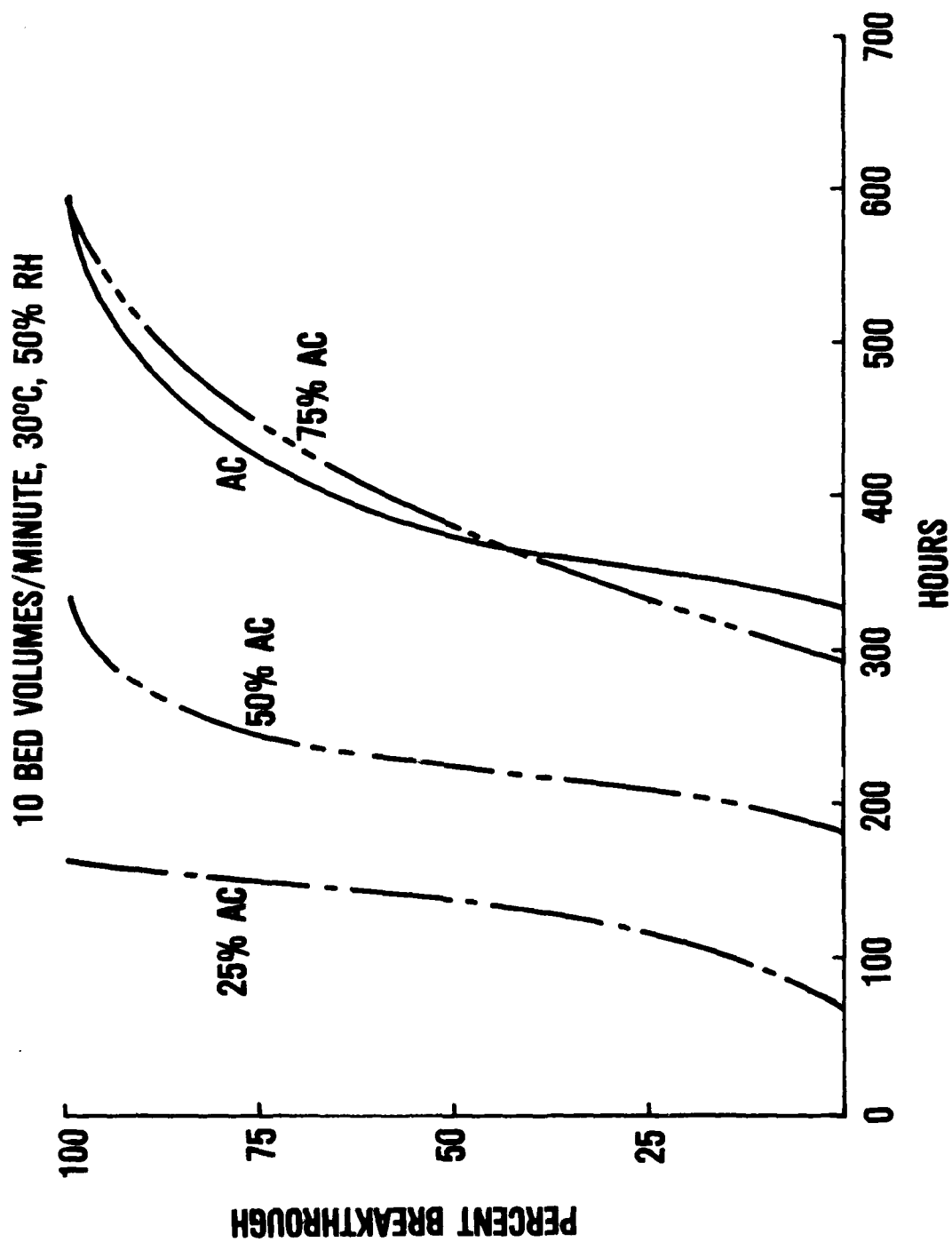


Figure 10A. Benzene breakthrough (100 ppm): AC charcoal/silica gel.

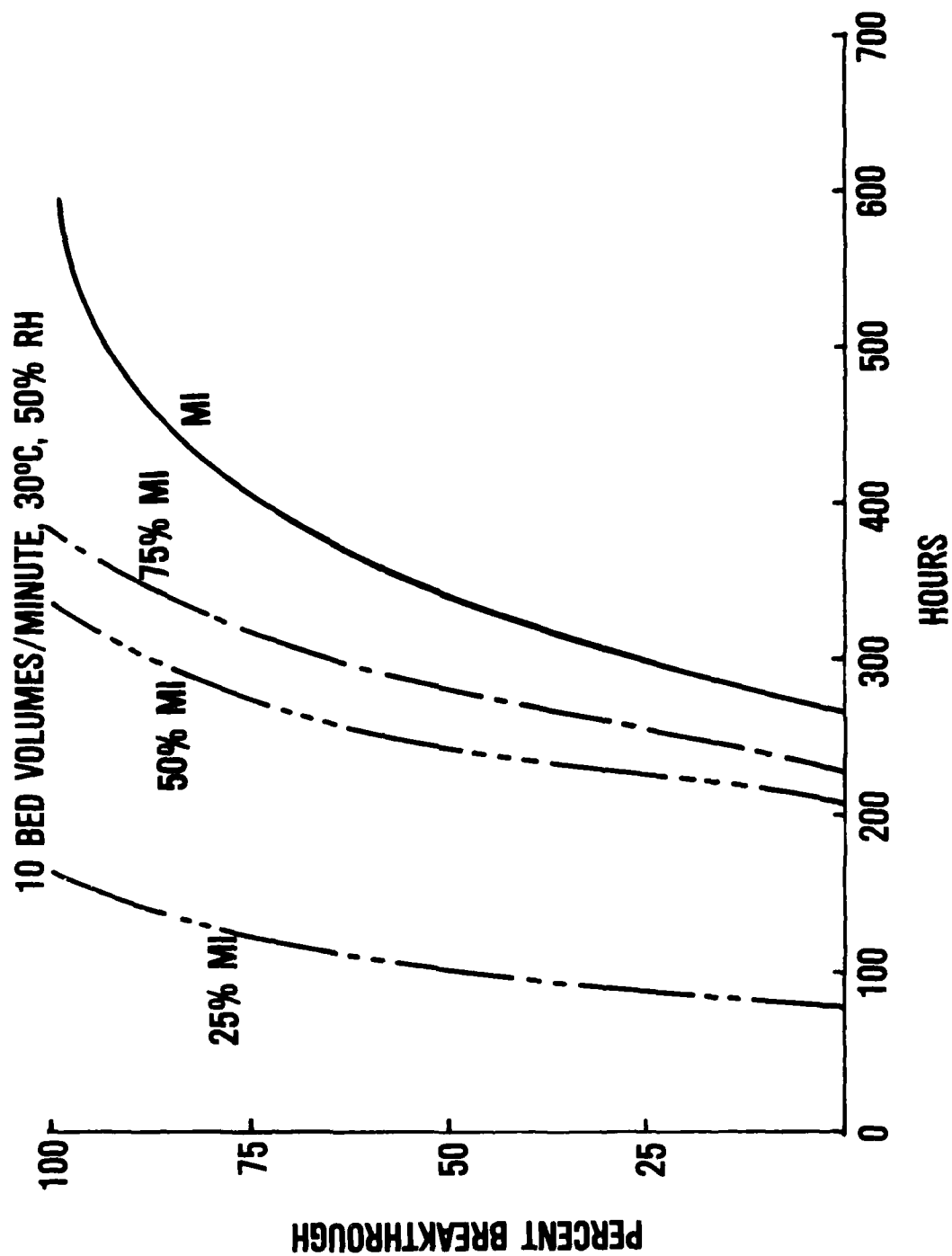
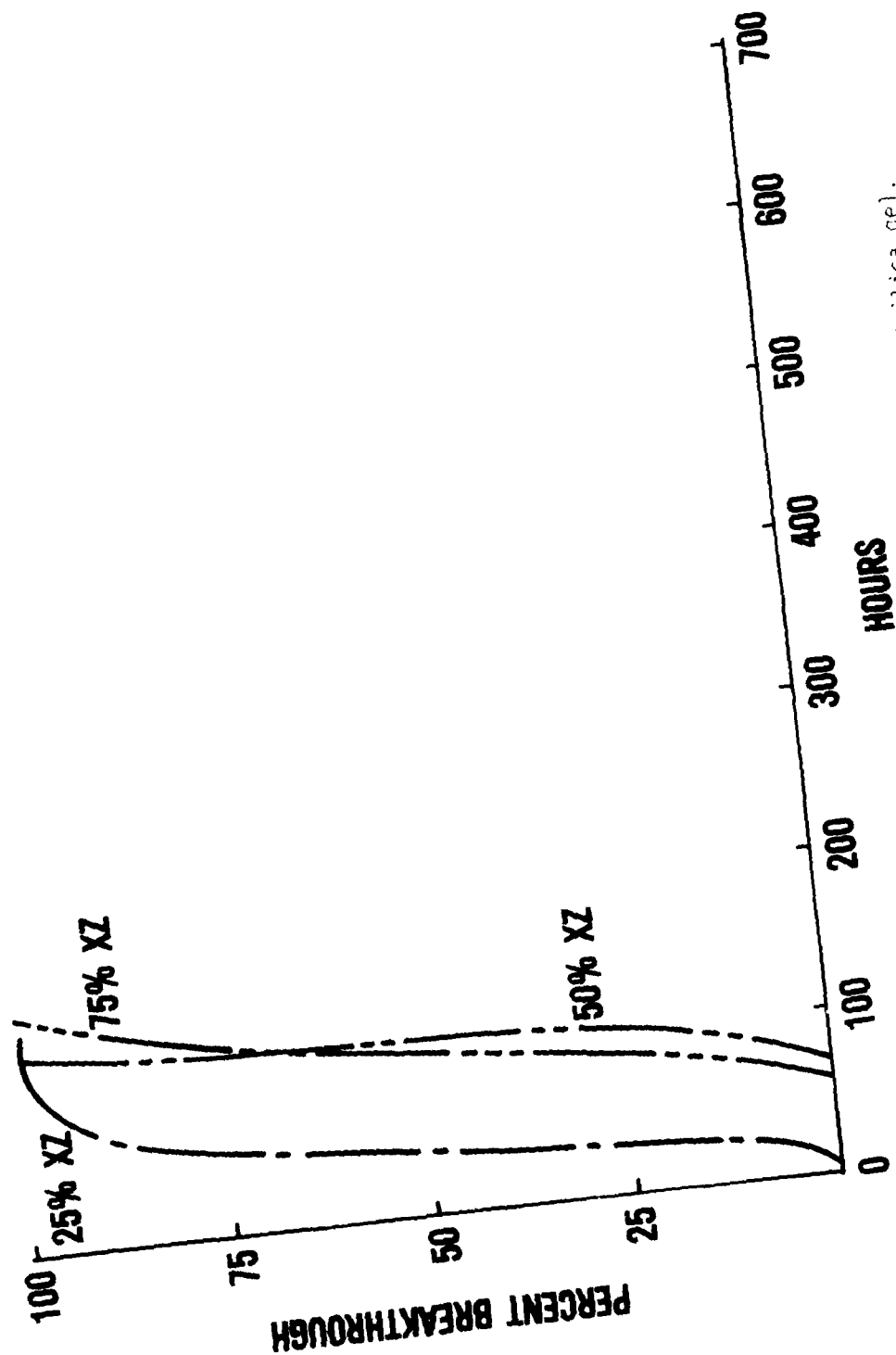


Figure 10B. Benzene breakthrough (100 ppm): MI charcoal/silica gel.

10 BED VOLUMES/MINUTE, 30°C, 50% RH



XZ charcoal/silica gel.

(100 ppm)

Figure 10c.

Benzene breakthrough

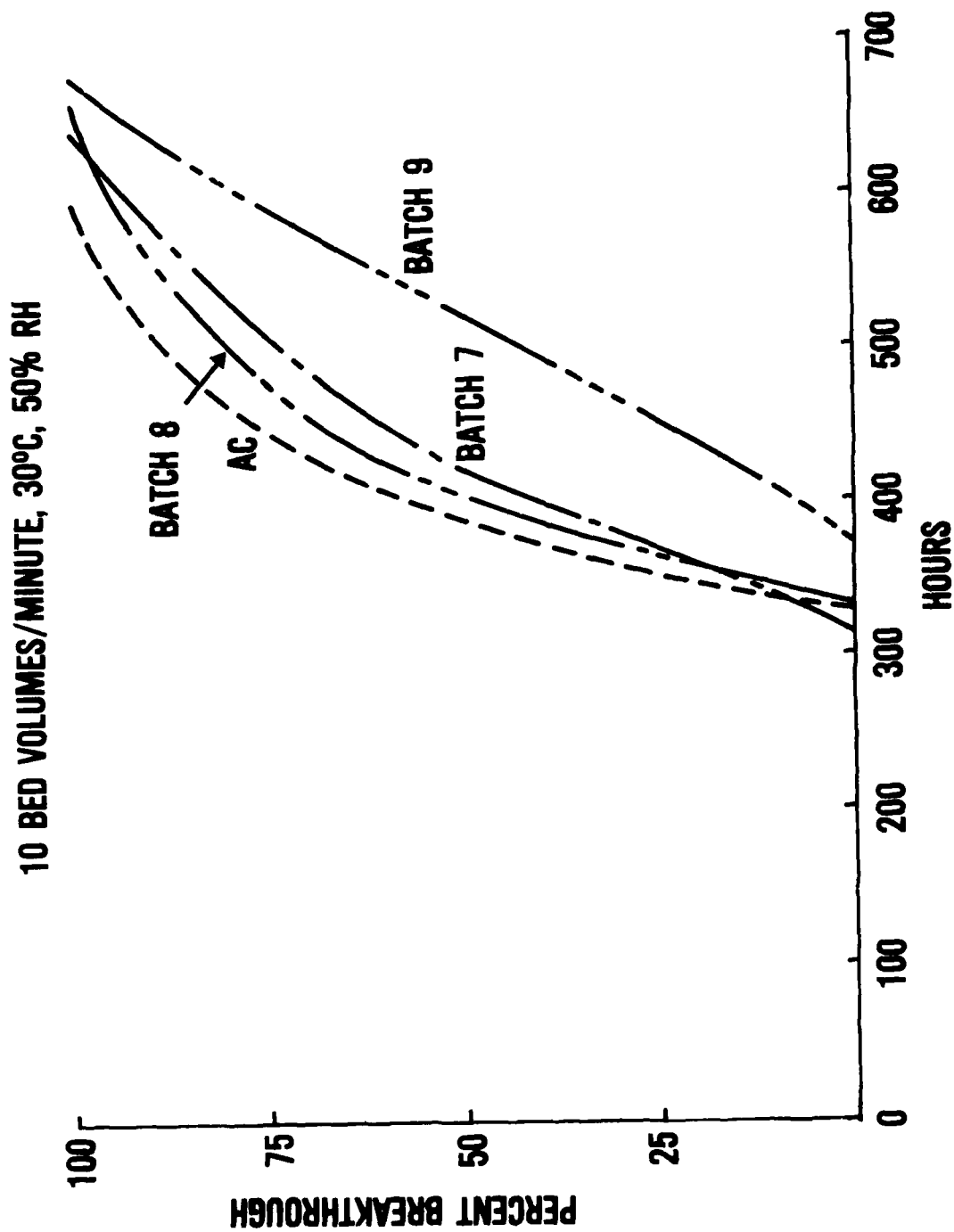


Figure 100. Benzene breakthrough (100 ppm): silica-gel-coated AC charcoal.

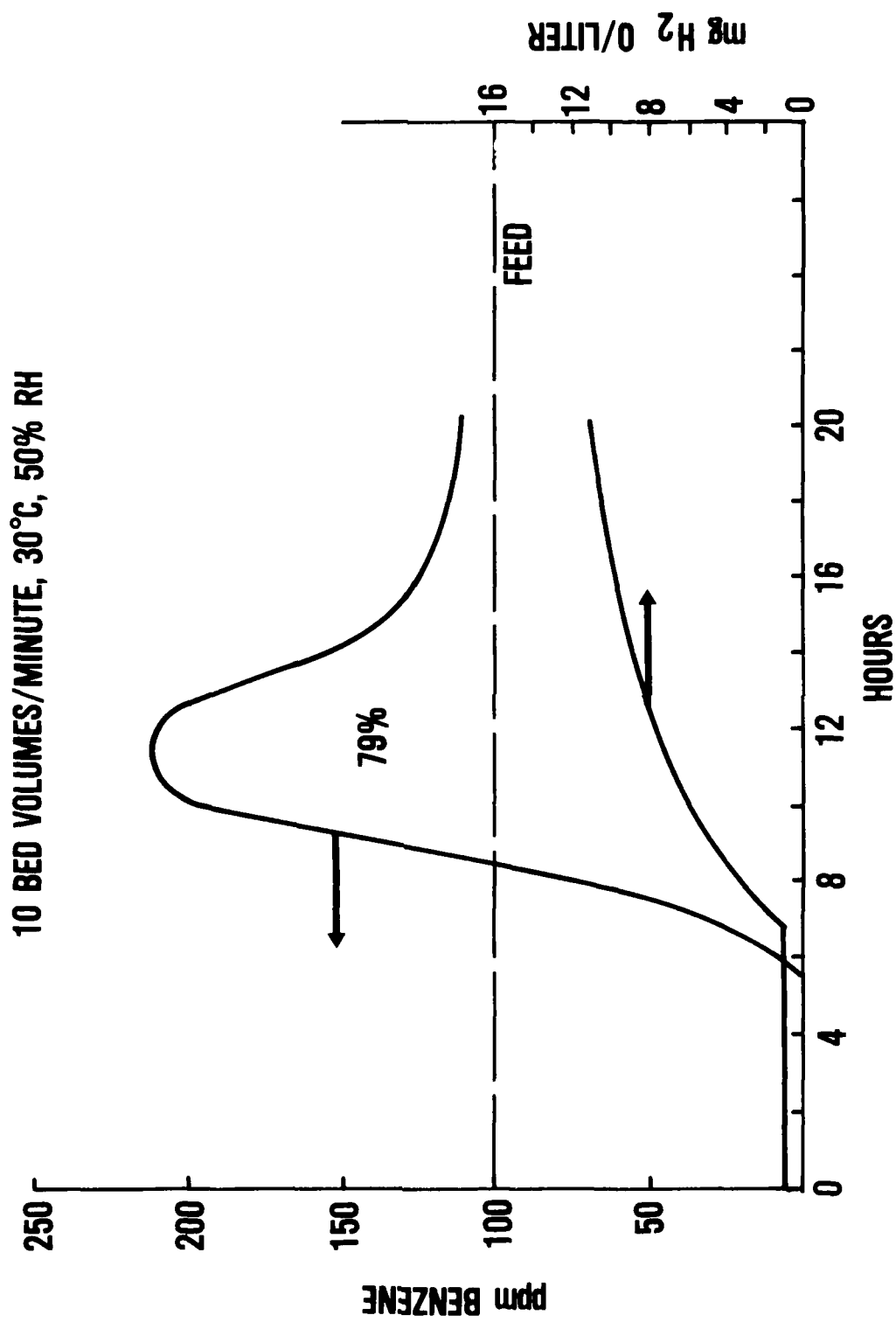


Figure 10E. Benzene breakthrough (100 ppm): silica gel.



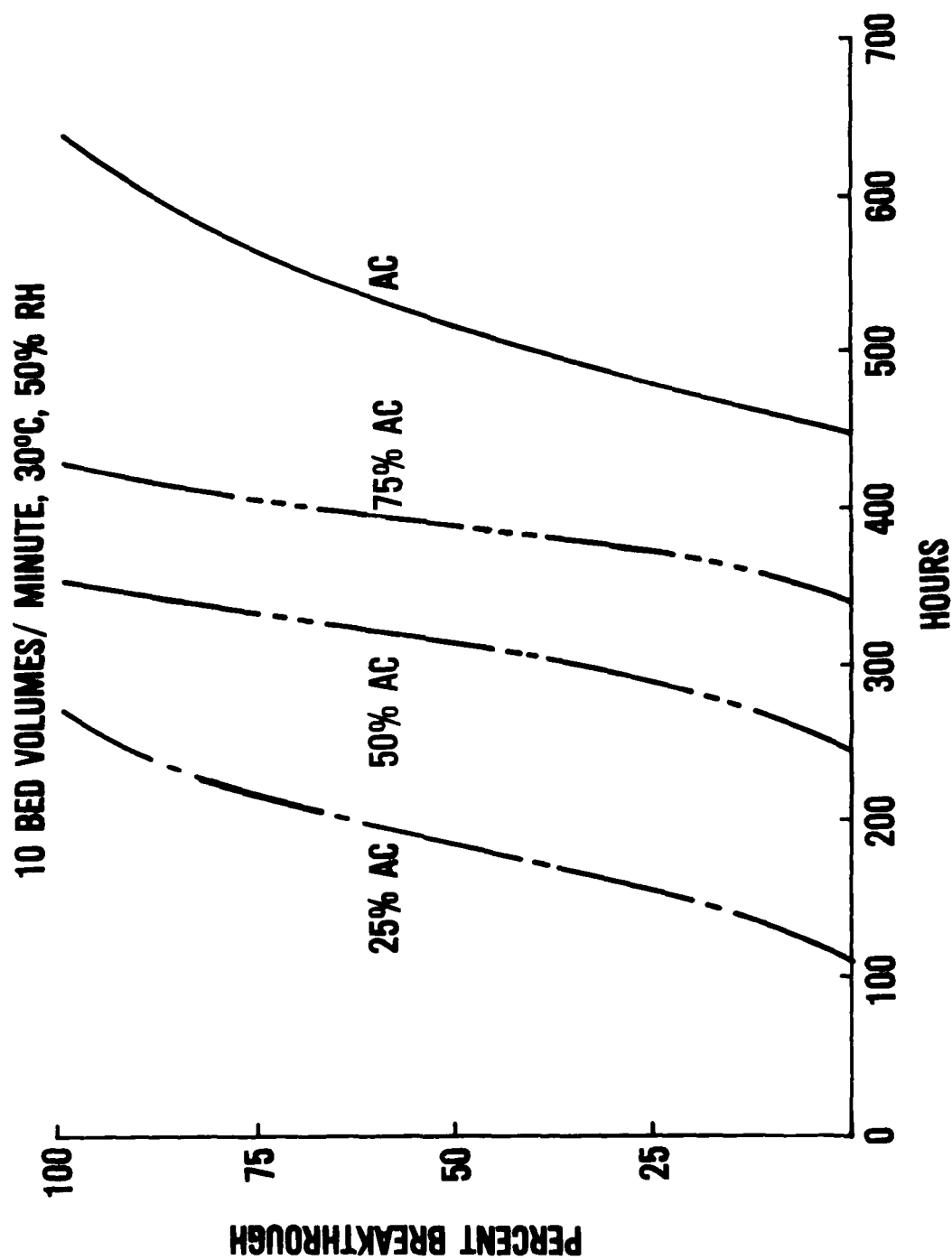


Figure 11A. Hexane breakthrough (80 ppm): AC charcoal/silica gel.

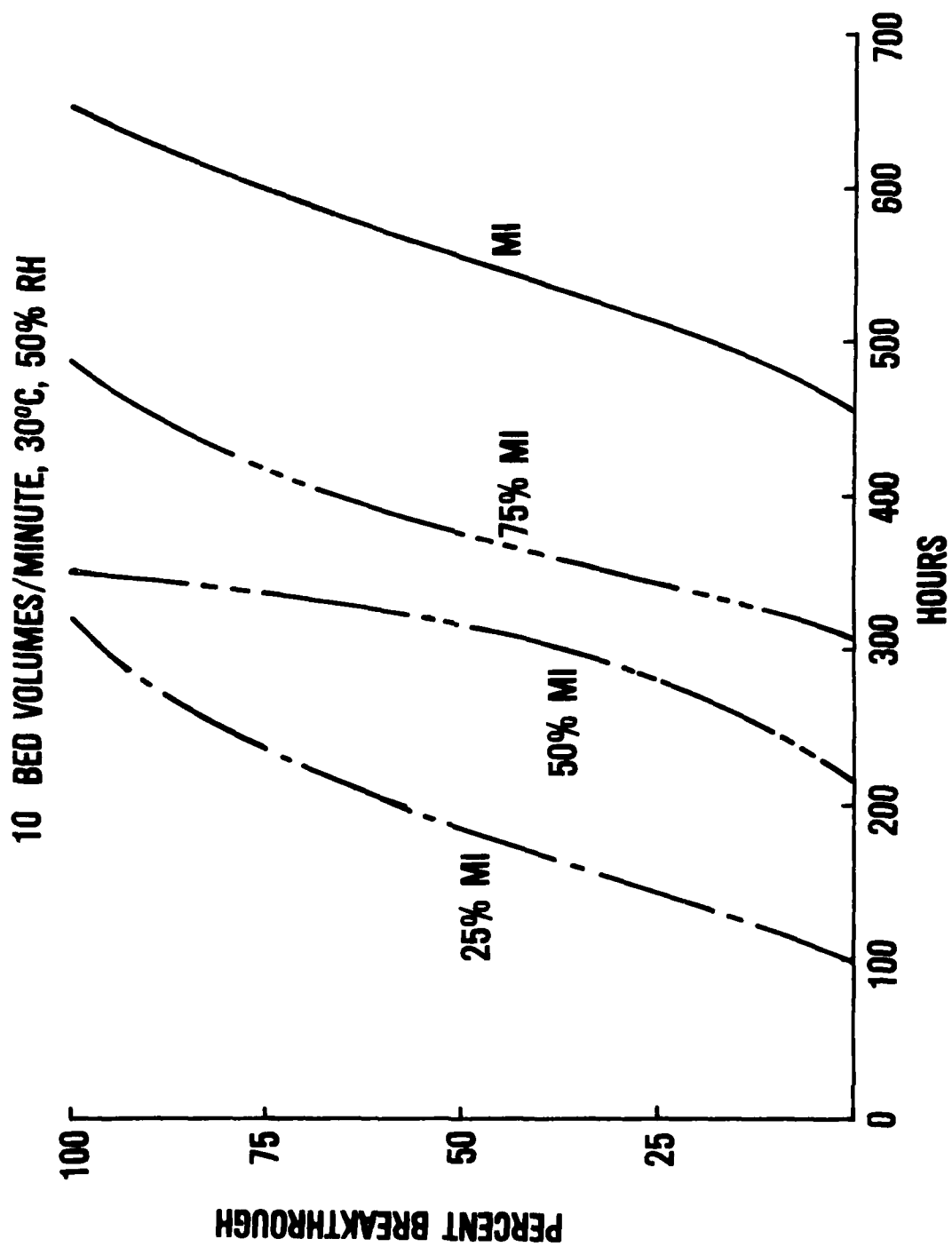


Figure 118. Hexane breakthrough (80 ppm): MI charcoal/silica gel.

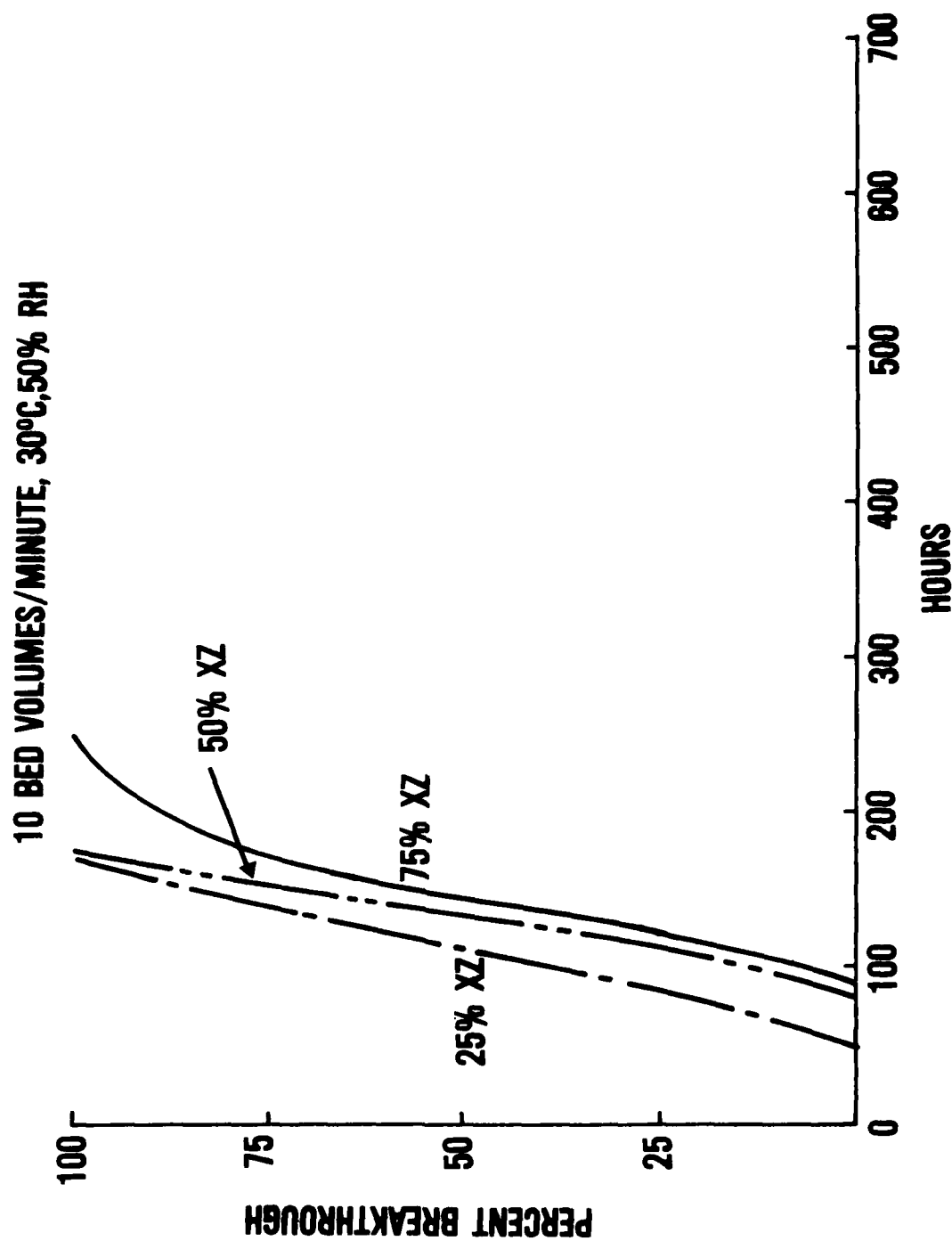


Figure 11C. Hexane breakthrough (80 ppm): XZ charcoal/silica gel.

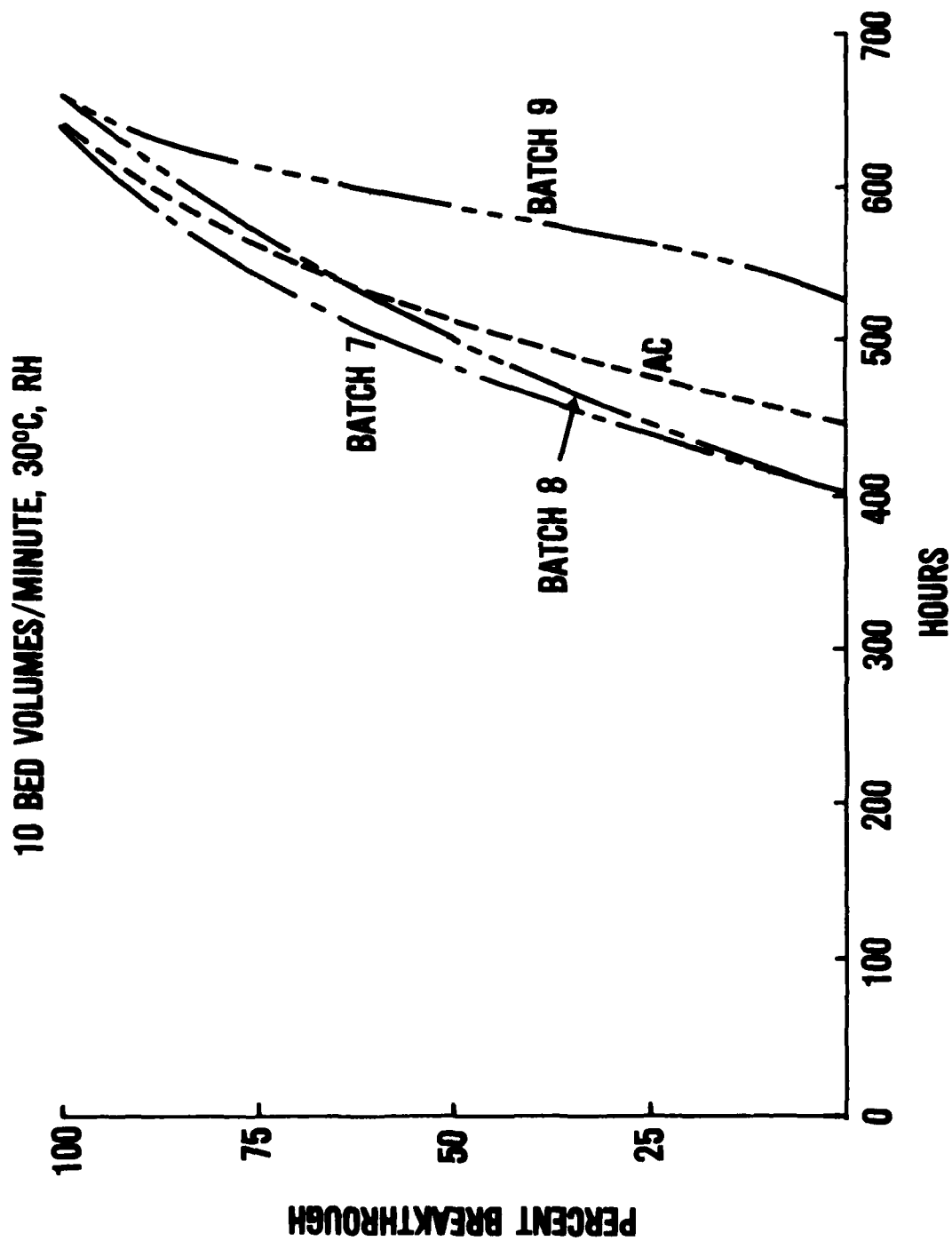


Figure 11D. Hexane breakthrough (80 ppm): silica-gel-coated AC charcoal.

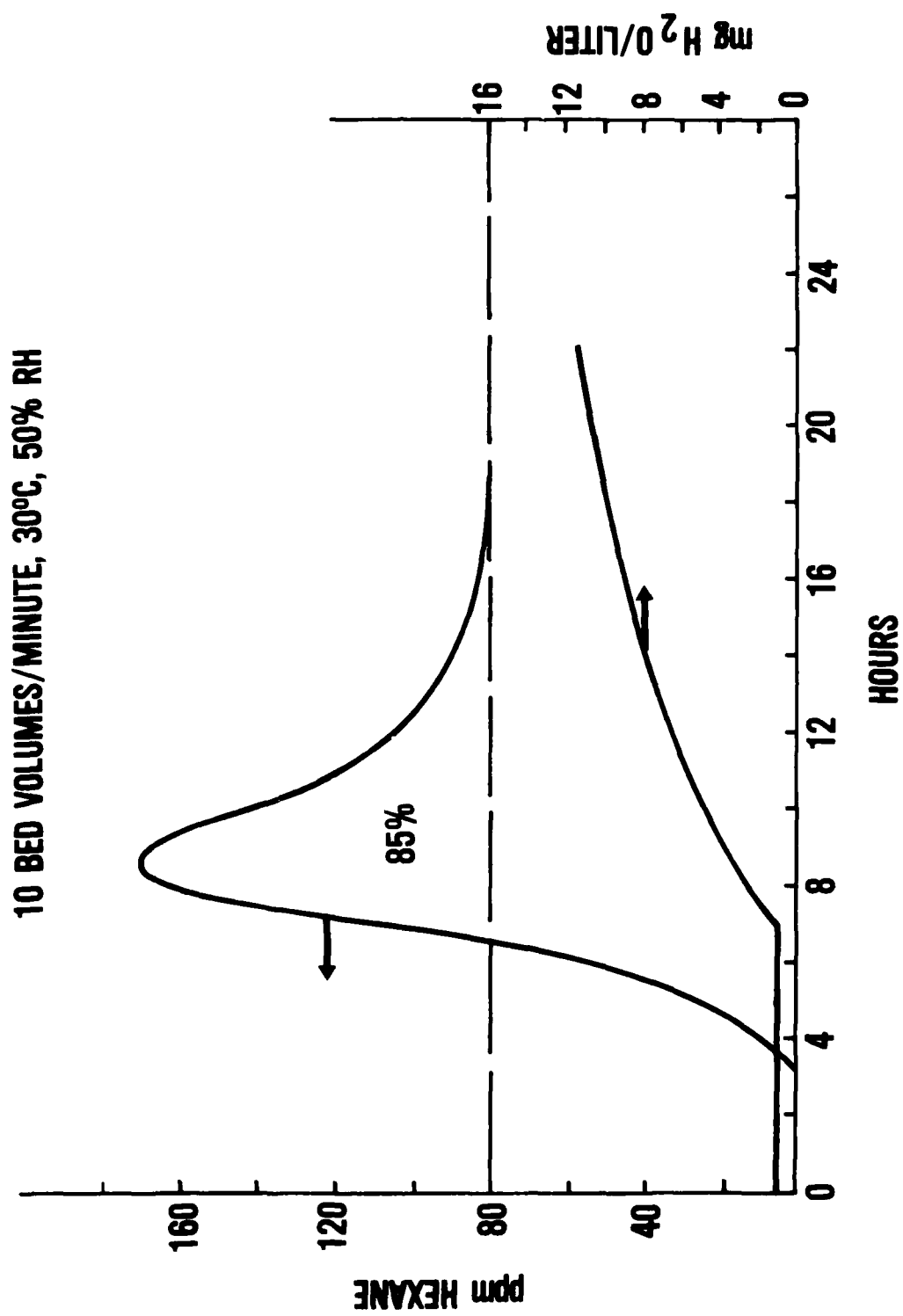


Figure 11E. Hexane breakthrough (80 ppm): silica gel.

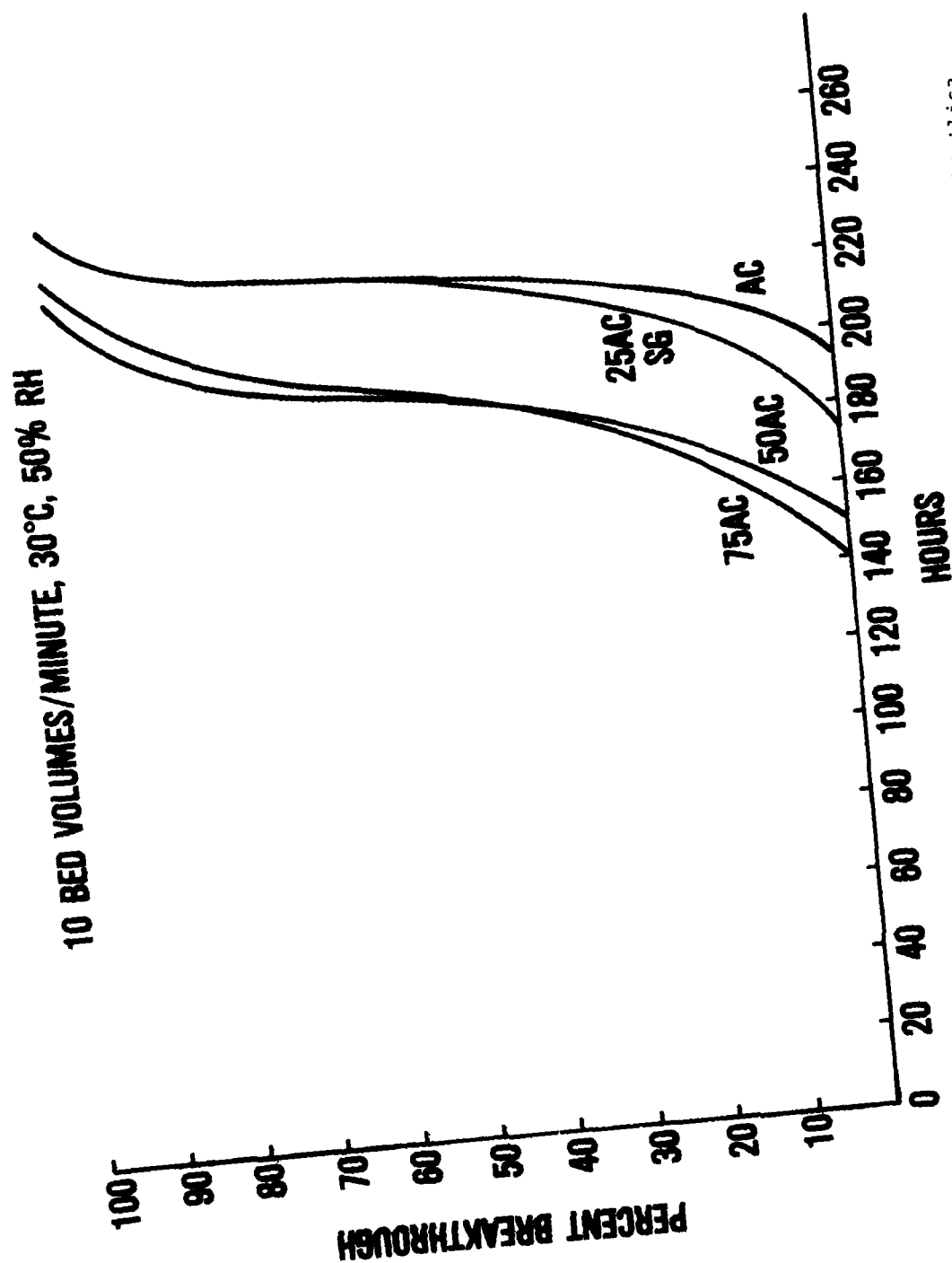


Figure 12A. Dimethyl methylphosphonate breakthrough (100 ppm): AC charcoal/silica gel mixtures.

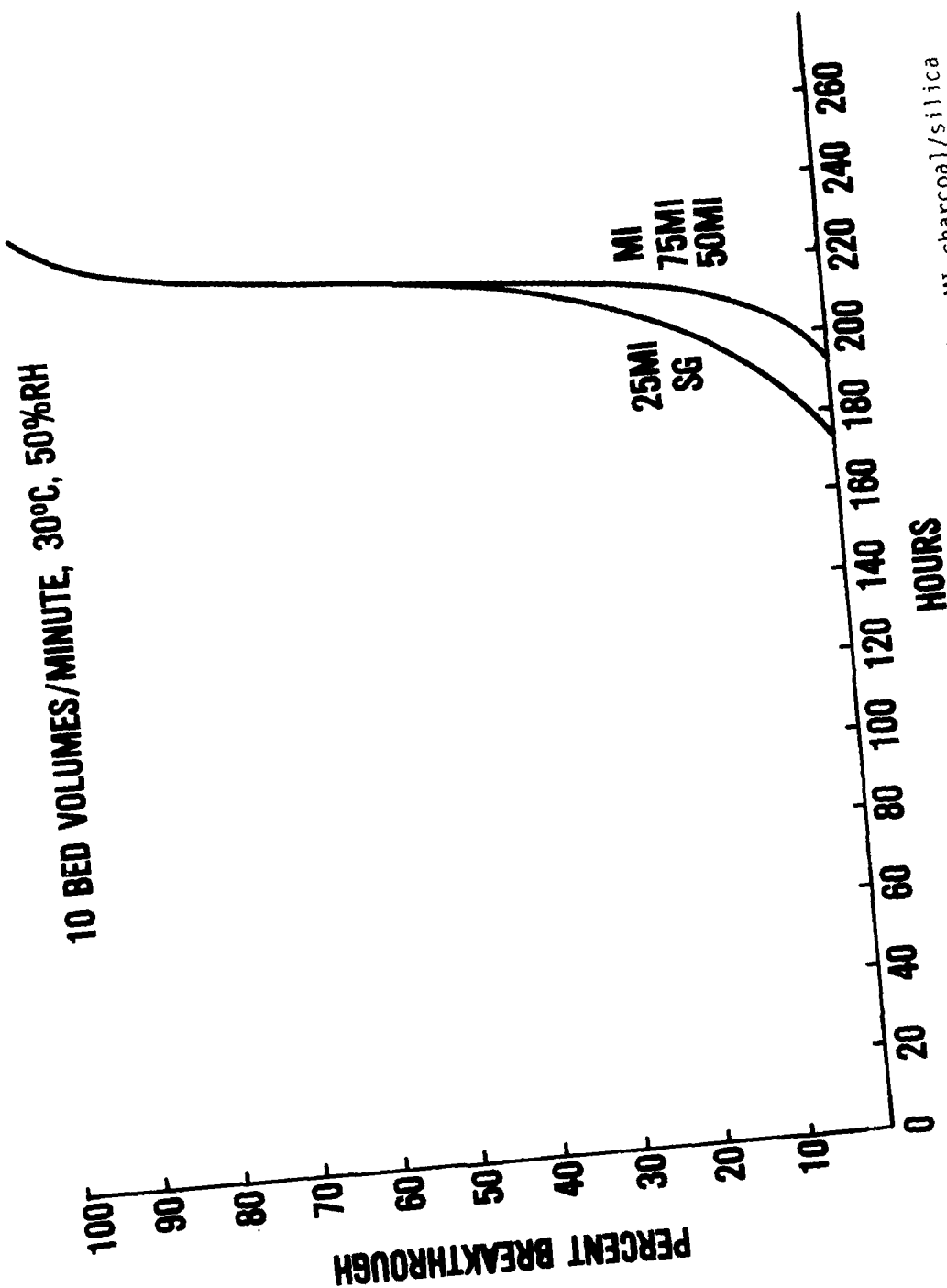


Figure 12B. Dimethyl methylphosphonate breakthrough (100 ppm): MI charcoal/silica gel mixtures.

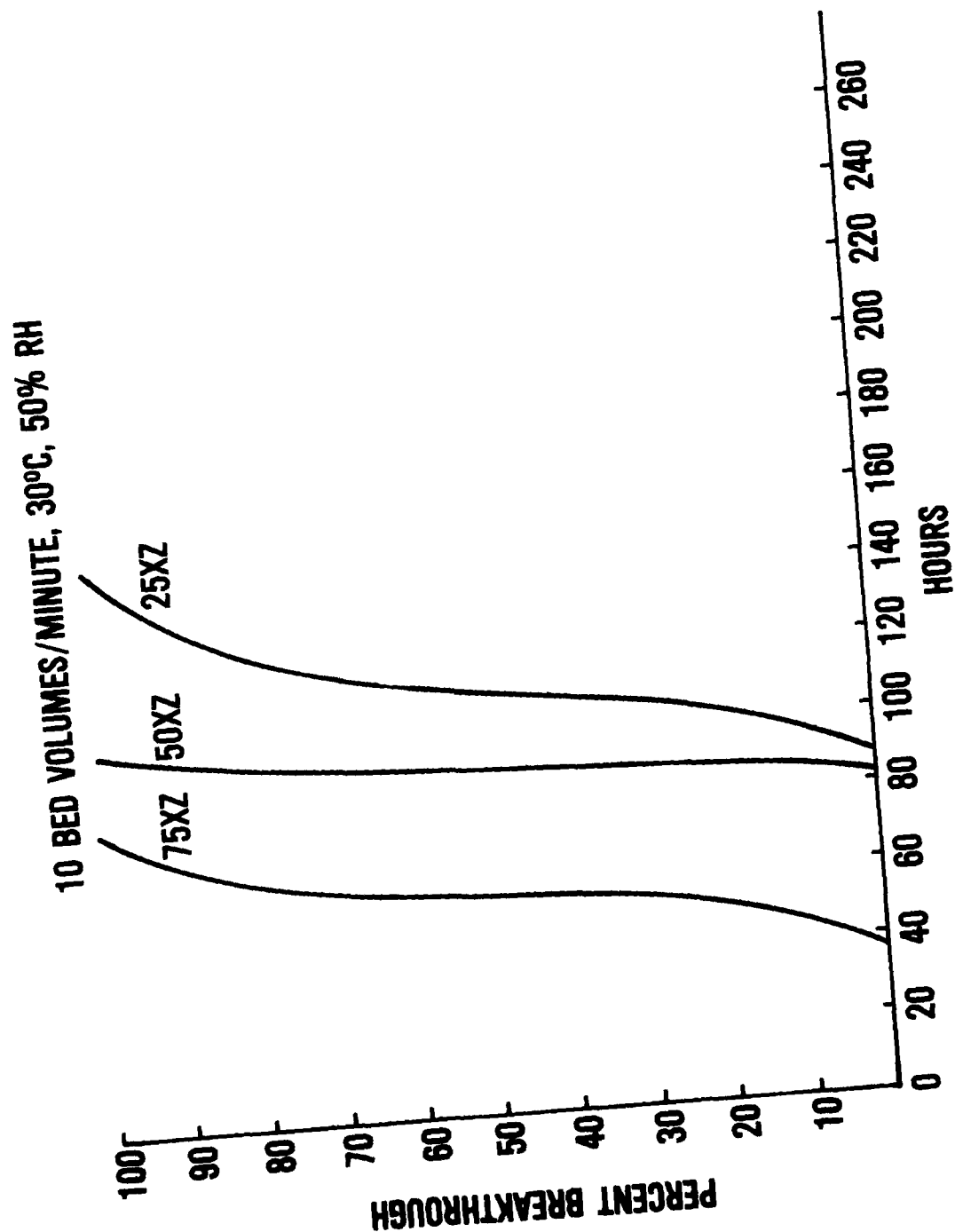


Figure 12C. Dimethyl methylphosphonate breakthrough (100 ppm): XZ charcoal coprecipitated with silica gel.



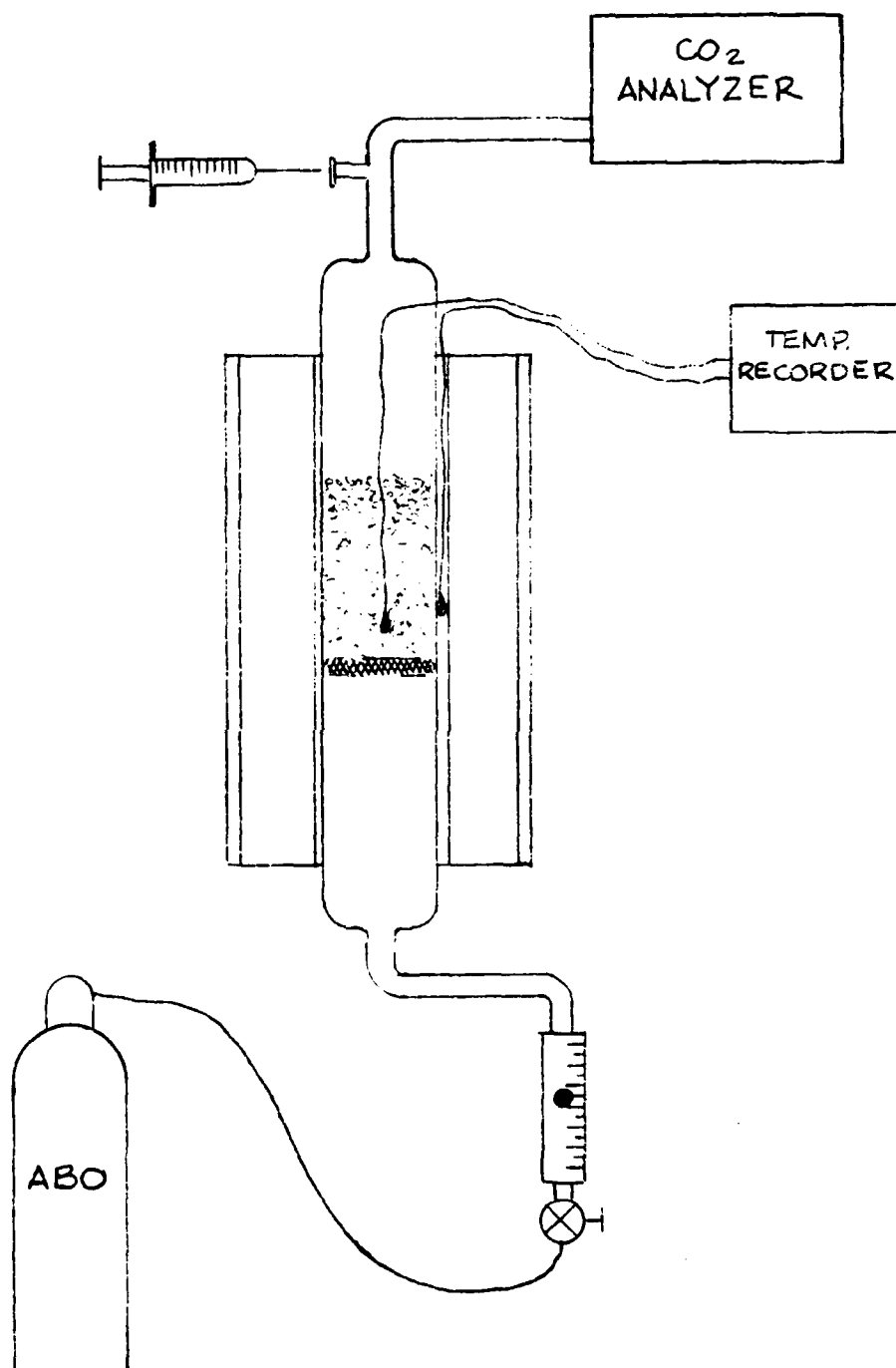


Figure 13. Ignition/Combustion test apparatus.

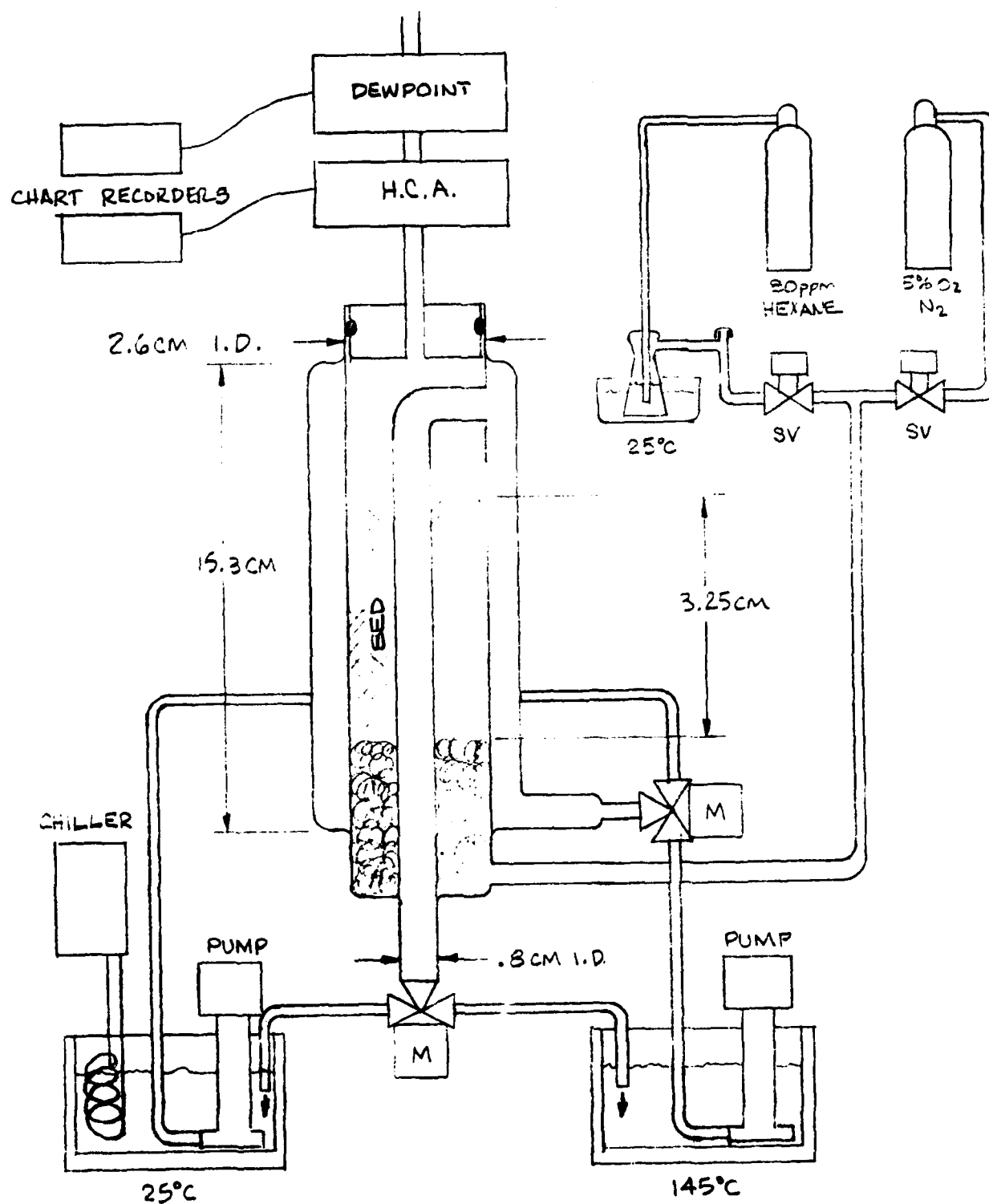


Figure 14. Regeneration test apparatus.

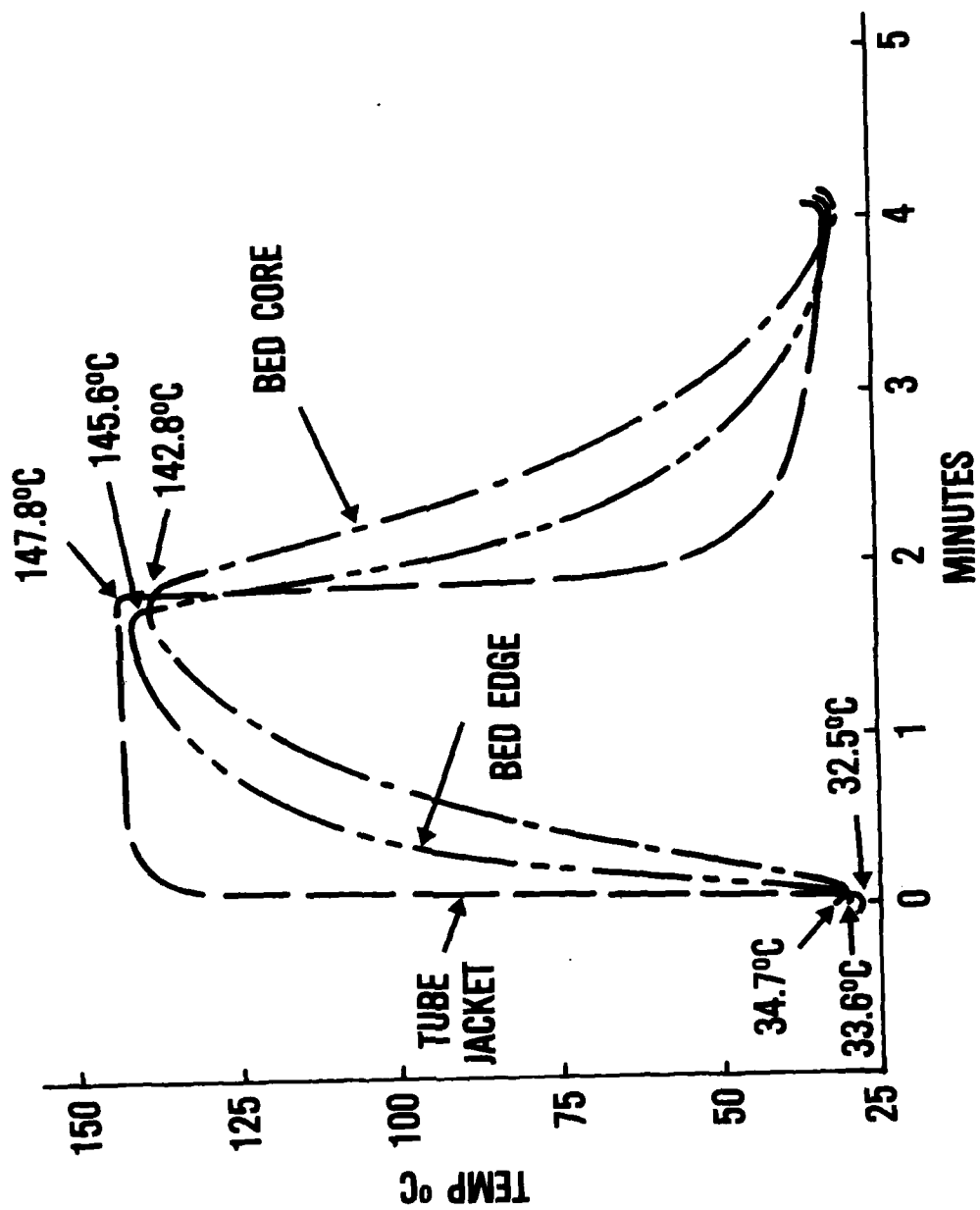


Figure 15. Regeneration temperatures.

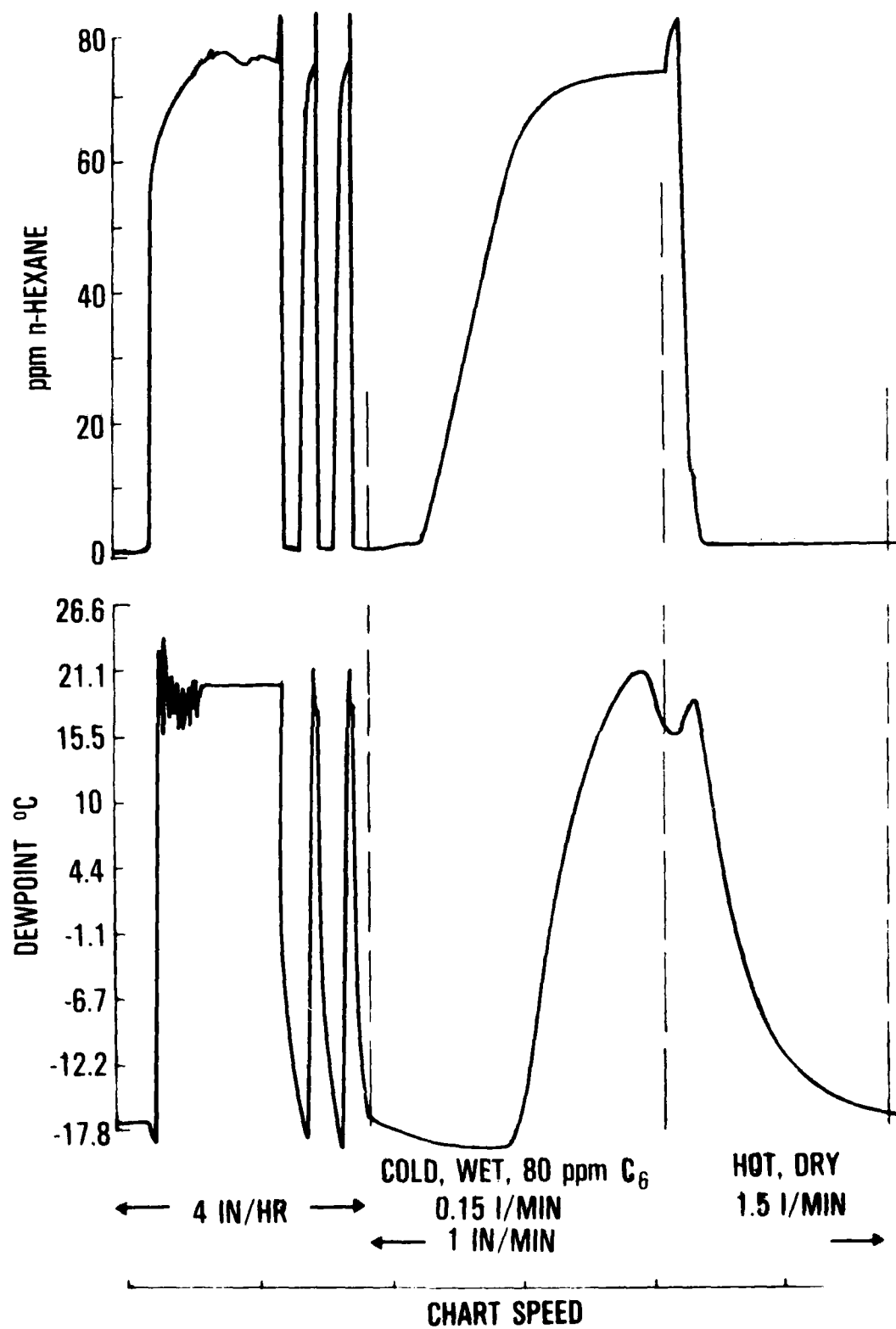


Figure 16. Instrument responses with empty housing.

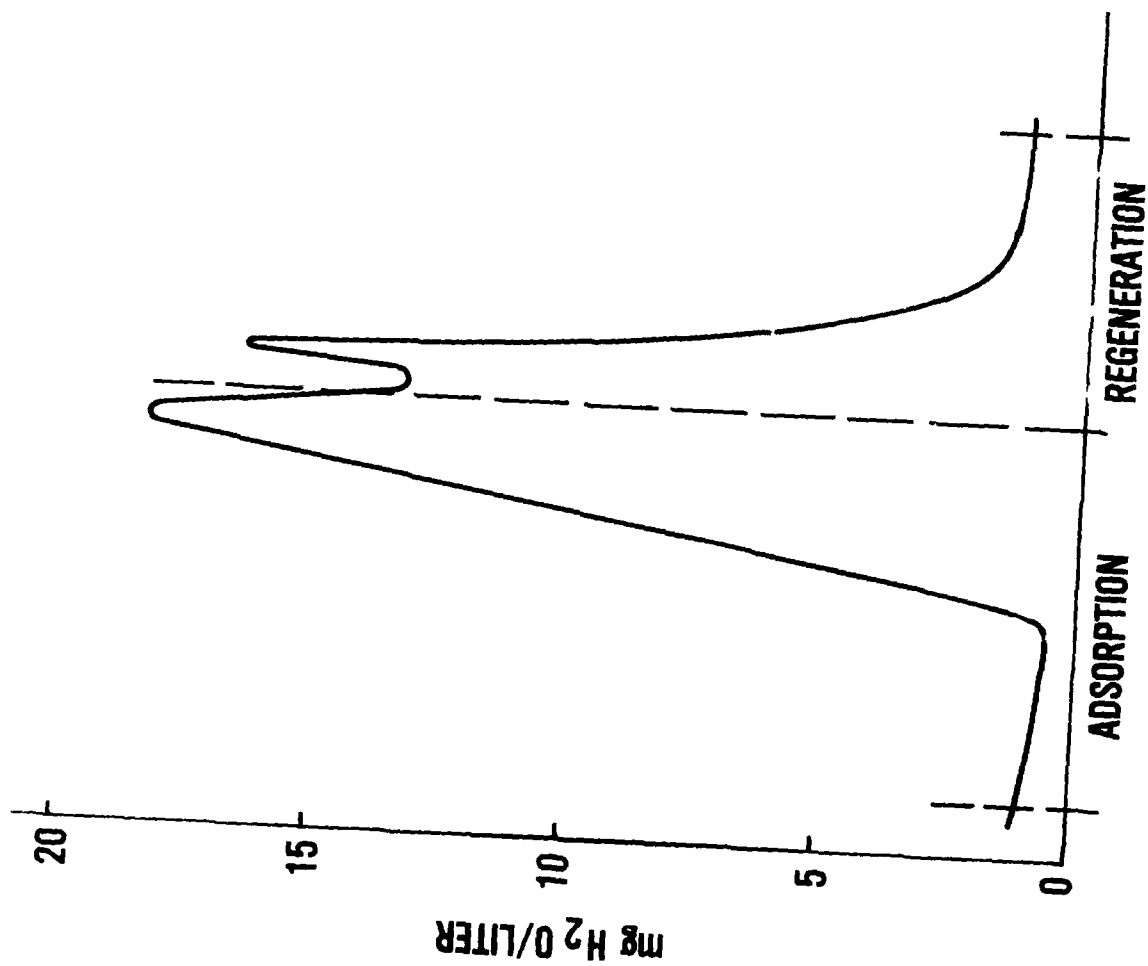


Figure 17. Dewpoint instrument response plotted as humidity.

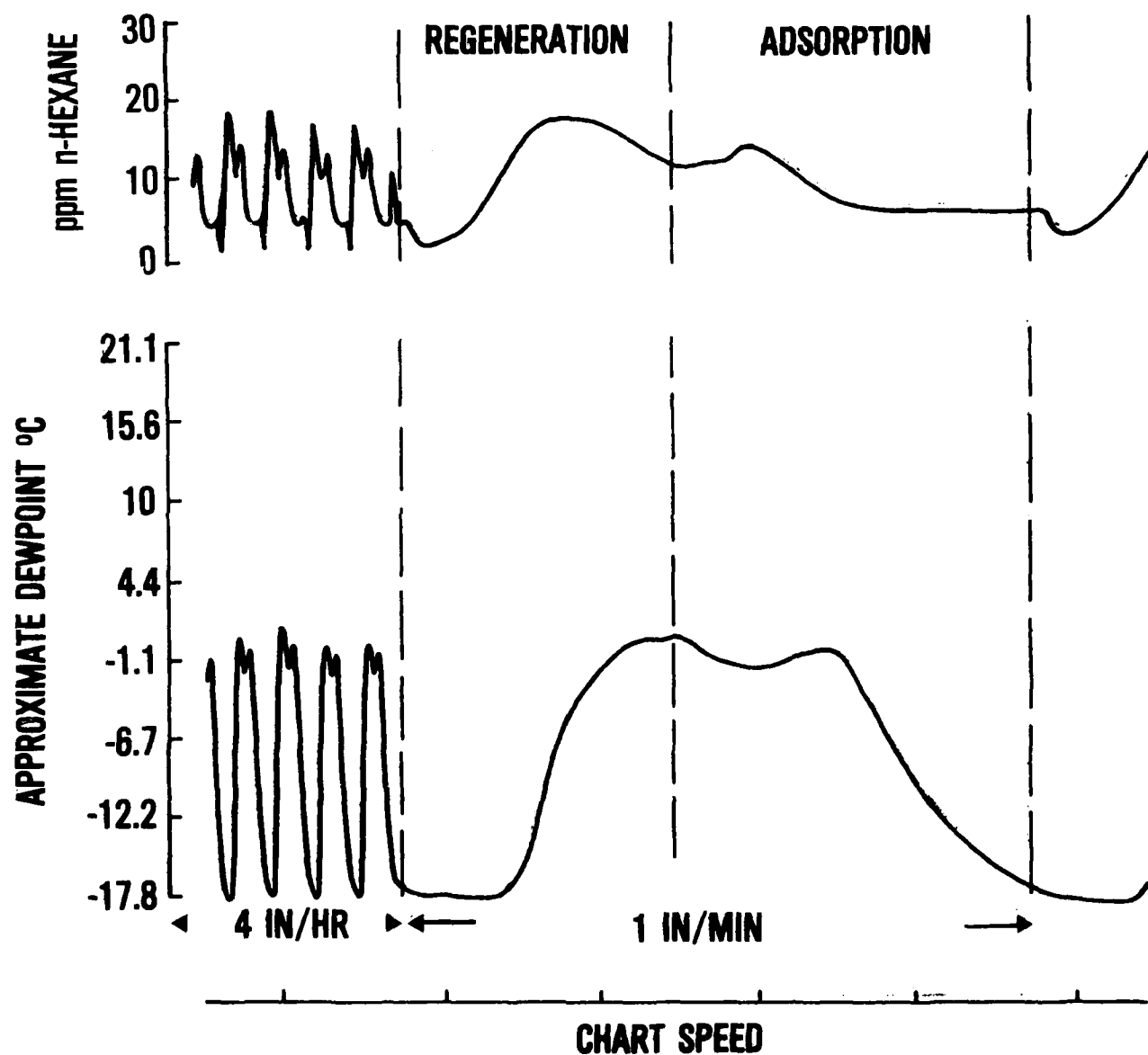


Figure 18. Silica gel regeneration cycles.

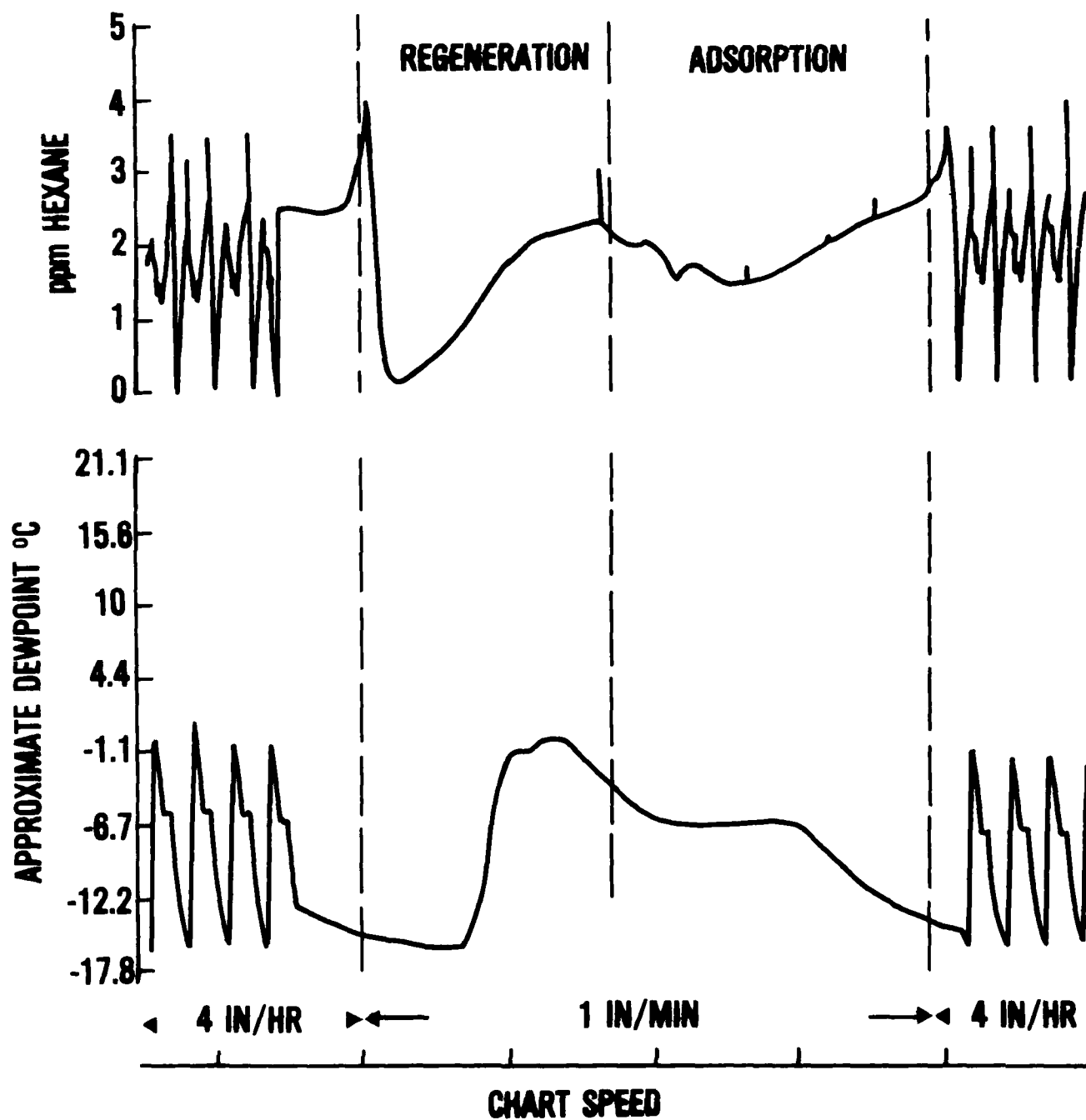


Figure 19A. Regeneration cycles (fresh bed): 40% MI charcoal.

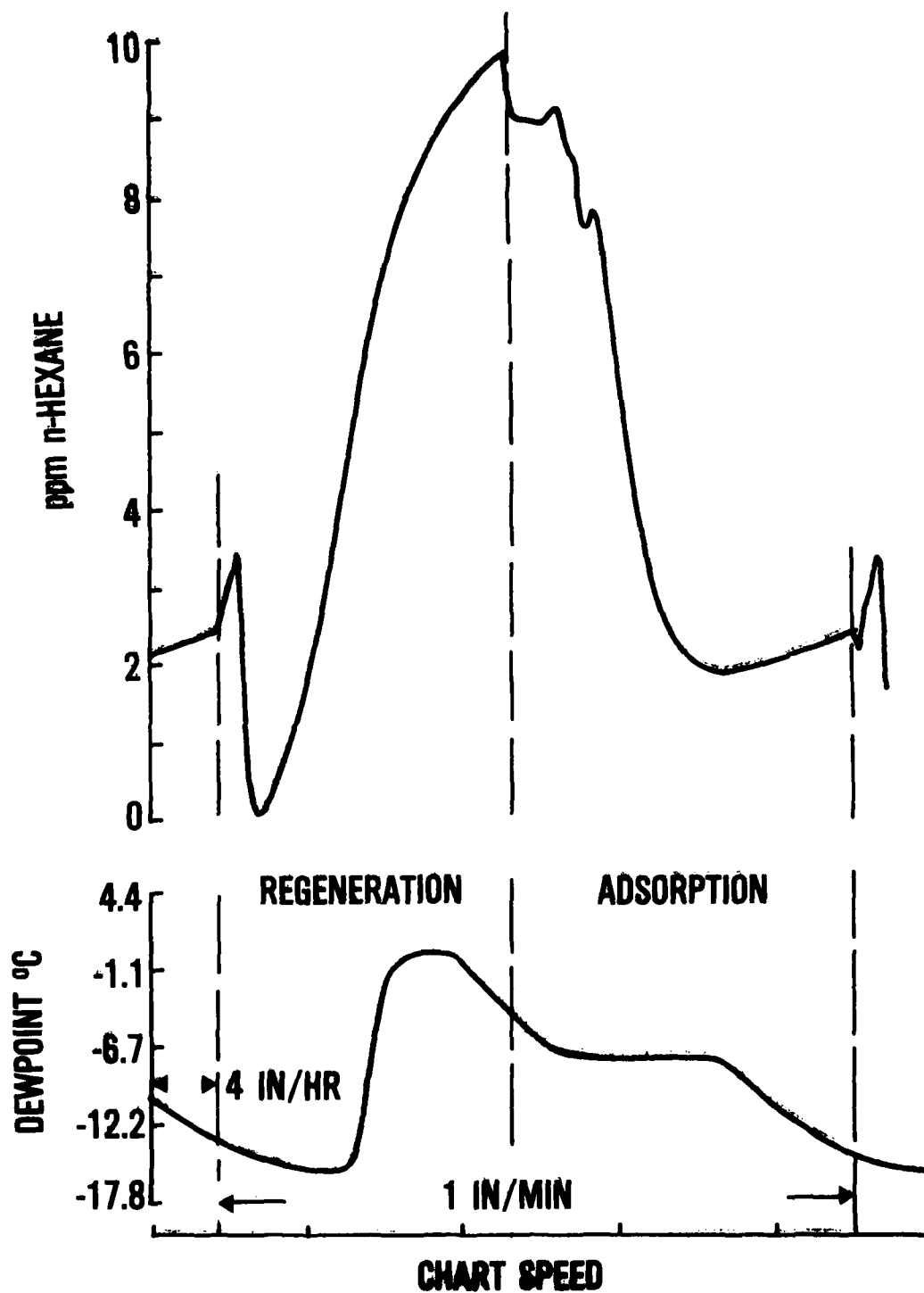


Figure 19B. Regeneration cycles (39.5 mg hexane added): 40% MI charcoal.



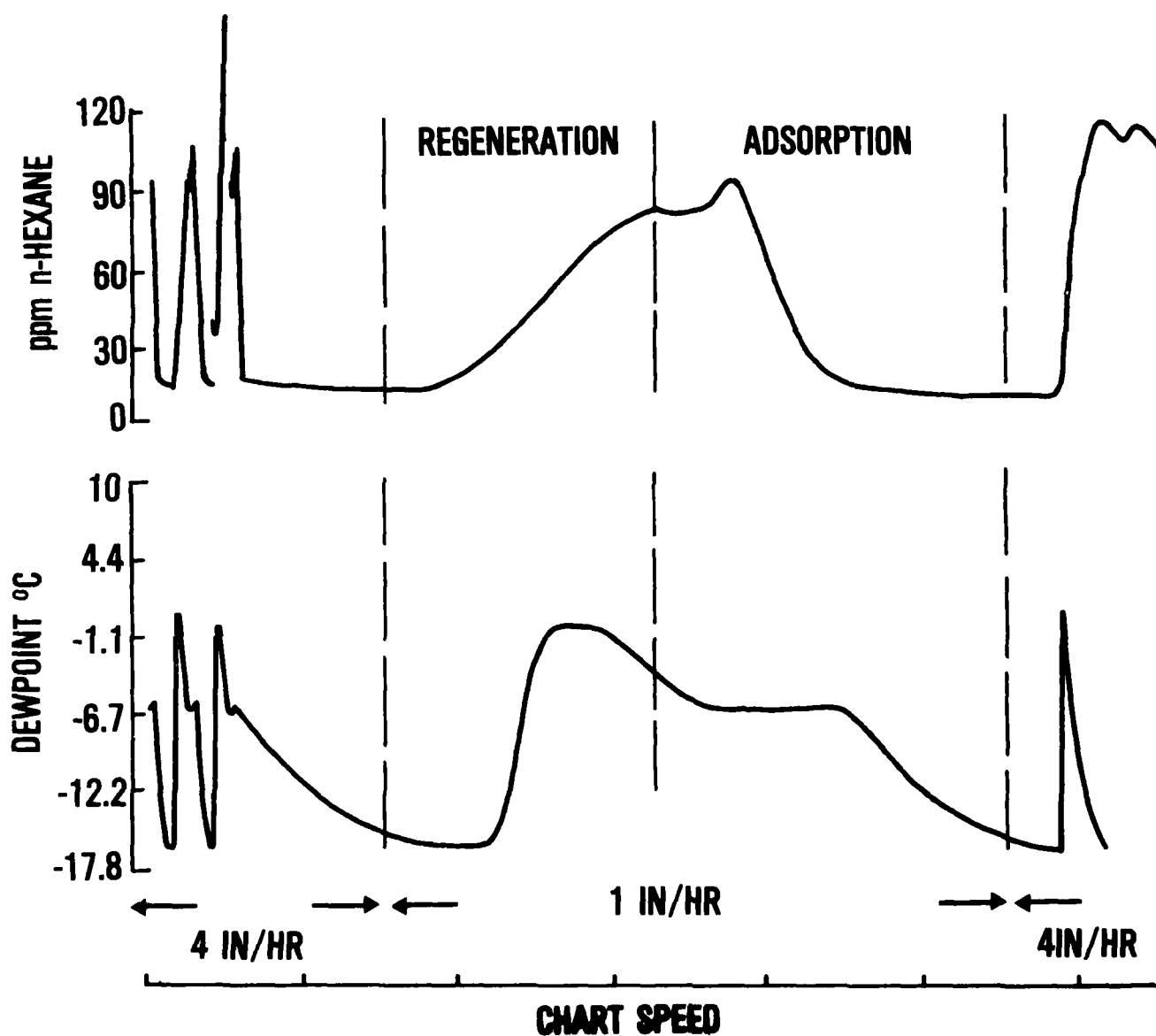


Figure 19C. Regeneration cycles (initially 0.7 g hexane added):  
40% AC charcoal.

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